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H. L. Jackson

H. L. JACKSON
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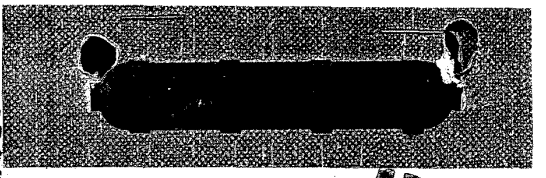

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SERIAL NUMBER	FILING DATE	CLASS	SUBCLASS	GROUP ART UNIT	EXAMINER
08/054,379	04/28/93	528	502	~~1503~~ 1505	

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Yes DW

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FOREIGN/PCT APPLICATIONS********
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35 USC 119 conditions met ☐ yes ☒ no								

ADDRESS

THE DOW CHEMICAL CO.
PATENT DEPARTMENT
BLDG. B-1211
DALLAS, TX 77541

TITLE

FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

U.S. DEPT. of COMM.-Pat. & TM Office — PTO-436L (rev. 10-78)

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ISSUE BATCH NUMBER	
PREPARED FOR ISSUE	

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Form PTO-436A (Rev. 8/92)

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Class	Subclass	ISSUE CLASSIFICATION
		08/378998

UTILITY SERIAL NUMBER 08/378998 | PATENT DATE | PATENT NUMBER ABANDONED

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APPLICANTS

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Yes, DW

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ADDRESS

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TITLE

FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

U.S. DEPT. of COMM.-Pat. & TM Office-PTO-436L (rev. 10-78)

PARTS OF APPLICATION FILED SEPARATELY

Applications Examiner

NOTICE OF ALLOWANCE MAILED

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Primary Examiner

Label Area

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(FACE)

9/13/93

PATENT APPLICATION SERIAL NO. 08/054379

U.S. DEPARTMENT OF COMMERCE
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Hon. Commissioner of Patents & Trademarks
Washington, D. C. 20231

Attorney's Case No. : C-40,121-G

Application of : Pak-Wing Steve Chum et. al

For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

No. of Drawing Sheets: 2

"Express Mail" mailing label number TB303883096
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B.	Extra Claims	10	x $22.00 =	220
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C.	Extra Independent Claims	1	x $74.00 =	74
D.	Multiple Dependent Claims Presented		+ $230.00 =	
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Respectfully submitted,
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Margaret Greene
(Typed or printed name of person mailing paper or fee)

Margaret Greene 378998
(Signature of person mailing paper or fee)

APPLICATION FOR LETTERS PATENT

Applicant(s): Pak-Wing Steve Chum, Ronald P. Markovich, George W. Knight, and Shih-Yaw Lai

Title: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

Attorney's Docket No.: C-40,121-G

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FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

Cross-Reference to Related Applications

This application is a continuation-in-part of pending application serial number 07/776,130, now USP 5,272,236, filed October 15, 1991 and is related to pending application serial number 07/939,281, now USP 5,278,272, entitled "Elastic Substantially Linear Olefin Polymers" filed September 2, 1992 in the names of Shih-Yaw Lai, George W. Knight, John R. Wilson and James C. Stevens, the disclosures of each of which is incorporated herein in their entirety by reference. This application is also related to pending application serial number 08/010,958, filed January 29, 1993 in the names of Brian W. S. Kolthammer and Robert S. Cardwell and entitled Ethylene Interpolymerizations, the disclosure of which is incorporated herein by reference.

Field of the Invention

This invention relates to compositions comprising specific ethylene/α-olefin polymer blends. The polymer blends preferably comprise:

(A) at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having specific processing characteristics, blended together with

(B) a heterogeneously branched ethylene polymer.

Such compositions are particularly useful in film applications (e.g., high strength thin gauge packaging film or heat sealable packaging film).

Background of the Invention

Thin film products fabricated from linear low density polyethylene (LLDPE) and/or high density polyethylene (HDPE) are widely used for packaging applications such as merchandise bags, grocery sacks, and industrial liners. For these applications, films with high tensile strength, as well as high impact strength, are desired

because film producers can down gauge their film products and still retain packaging performance.

Previous attempts were made to optimize film tensile strength and yield strength by blending various heterogeneous polymers together on theoretical basis. While such blends exhibited a synergistic response to increase the film yield strength, the film impact strength followed the rule of mixing, often resulting in a "destructive synergism" (i.e., the film impact strength was actually lower than film made from one of the two components used to make the blend).

For example, it is known that while improved modulus linear polyethylene resin can be produced by blending high density polyethylene with a very low density polyethylene (VLDPE), the impact strength of the resin blend follows the rule of mixing.

There is a continuing need to develop polymers which can be formed into fabricated articles (e.g., film) having these combinations of properties (e.g., improved modulus, yield strength, impact strength and tear strength). The need is especially great for polymers which can be made into film which can also be down gauged without loss of strength properties, resulting in savings for film manufacturers and consumers, as well as protecting the environment by source reduction.

Surprisingly, we have now discovered that film can have synergistically enhanced physical properties, when the film is made from a blend of at least one homogeneously branched ethylene/α-olefin interpolymer and a heterogeneously branched ethylene/α-olefin interpolymer.

Brief Description of the Drawings

Figure 1 shows the relationship between the density and the slope of strain hardening coefficient for homogeneously branched substantially linear ethylene/α-olefin interpolymers used in the compositions disclosed herein, in comparison with a heterogeneously branched ethylene/α-olefin copolymer.

Figure 2 shows the short chain branching distribution (as measured by analytical temperature rising elution fractionation (ATREF)) for a homogeneously branched substantially linear ethylene/1-octene copolymer used in the invention, in comparison with Dowlex™ 2045 (a heterogeneously branched ethylene/1-octene copolymer made by The Dow Chemical Company).

Summary of the Invention

Formulated ethylene/α-olefin compositions have now been discovered to have improved physical and mechanical strength and are useful in making fabricated articles. Films made from these novel compositions exhibit surprisingly good impact and tensile properties, and an especially good combination of modulus , yield, ultimate tensile, and toughness (e.g. Dart impact).

The compositions comprise from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of

~~(A)~~ at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min) to about 10 g/10 min,

(iv) no linear polymer fraction, and

(v) a single melting peak as measured using differential scanning calorimetry; and

(B) at least one heterogeneously branched ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3.

In another aspect, the compositions comprise from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of :

(A) at least one homogeneously branched linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_W/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min) to about 10 g/10 min,

(iv) no linear polymer fraction, and

(v) a single melting peak as measured using differential scanning calorimetry; and

(B) at least one heterogeneously branched ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3.

Preferably, both the homogeneously branched substantially linear ethylene/α-olefin interpolymer and the homogeneously branched linear ethylene/α-olefin interpolymer each have a slope of strain hardening coefficient greater than or equal to about 1.3.

Detailed Description of the Invention

The homogeneously branched ethylene/α-olefin interpolymer is preferably a homogeneously branched substantially linear ethylene/α-olefin interpolymer as described in pending USSN 07/776,130. The homogeneously branched ethylene/α-olefin interpolymer can also be a linear ethylene/α-olefin interpolymer as described in USP 3,645,992 (Elston), the disclosure of which is incorporated herein by reference.

The substantially linear ethylene/α-olefin interpolymers are not "linear" polymers in the traditional sense of the term, as used to describe linear low density polyethylene (e.g., Ziegler polymerized linear low density polyethylene (LLDPE)), nor are they highly branched polymers, as used to describe low density polyethylene (LDPE).

The substantially linear ethylene/α-olefin interpolymers of the present invention are herein defined as in copending application serial number 07/776,130 and in copending application entitled "Elastic

Substantially Linear Olefin Polymers" filed September 2, 1992 in the names of Shih-Yaw Lai, George W. Knight, John R. Wilson and James C. Stevens.

The homogeneously branched ethylene/α-olefin interpolymers useful for forming the compositions described herein are those in which the comonomer is randomly distributed within a given interpolymer molecule and wherein substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer. The homogeneity of the interpolymers is typically described by the SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) and is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, in Wild et al, Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), in U.S. Patent 4,798,081 (Hazlitt et al.), or in U.S. Patent 5,089,321 (Chum et al.) the disclosures of all of which are incorporated herein by reference. The SCBDI or CDBI for the linear and for the substantially linear olefin polymers of the present invention is preferably greater than about 30 percent, especially greater than about 50 percent. The homogeneous ethylene/α-olefin polymers used in this invention essentially lack a measurable "high density" fraction as measured by the TREF technique (i.e., the homogeneously branched ethylene/α-olefin polymers do not contain a polymer fraction with a degree of branching less than or equal to 2 methyls/1000 carbons). The homogeneously branched ethylene/α-olefin polymers also do not contain any highly short chain branched fraction (i.e., the homogeneously branched ethylene/α-olefin polymers do not contain a polymer fraction with a degree of branching equal to or more than about 30 methyls/1000 carbons).

The substantially linear ethylene/α-olefin interpolymers for use in the present invention typically are interpolymers of ethylene

with at least one C_3-C_{20} α-olefin and/or C_4-C_{18} diolefins. Copolymers of ethylene and 1-octene are especially preferred. The term "interpolymer" is used herein to indicate a copolymer, or a terpolymer, or the like. That is, at least one other comonomer is polymerized with ethylene to make the interpolymer. Ethylene copolymerized with two or more comonomers can also be used to make the homogeneously branched substantially linear interpolymers useful in this invention. Preferred comonomers include the C_3-C_{20} α-olefins, especially propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, and 1-decene, more preferably 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

The term "linear ethylene/α-olefin interpolymer" means that the interpolymer does not have long chain branching. That is, the linear ethylene/α-olefin interpolymer has an absence of long chain branching, as for example the linear low density polyethylene polymers or linear high density polyethylene polymers made using uniform (i.e., homogeneous) branching distribution polymerization processes (e.g., as described in USP 3,645,992 (Elston)) and are those in which the comonomer is randomly distributed within a given interpolymer molecule and wherein substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer. The term "linear ethylene/α-olefin interpolymer" does not refer to high pressure branched (free-radical polymerized) polyethylene which is known to those skilled in the art to have numerous long chain branches. The branching distribution of the homogeneously branched linear ethylene/α-olefin interpolymers is the same or substantially the same as that described for the homogeneously branched substantially linear ethylene/α-olefin interpolymers, with the exception that the linear ethylene/α-olefin interpolymers do not have any long chain branching. The homogeneously branched linear ethylene/α-olefin interpolymers comprise ethylene with at least one C_3-C_{20} α-olefin and/or C_4-C_{18} diolefin. Copolymers of ethylene and 1-octene are especially preferred. Preferred comonomers include the C_3-C_{20} α-olefins, especially propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-

pentene, 1-heptene, 1-octene, 1-nonene, and 1-decene, more preferably 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

Both the homogeneously branched substantially linear and linear ethylene/α-olefin interpolymers have a single melting point, as opposed to traditional heterogeneously branched Ziegler polymerized ethylene/α-olefin copolymers having two or more melting points, as determined using differential scanning calorimetry (DSC).

The density of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers (as measured in accordance with ASTM D-792) for use in the present invention is generally from about 0.89 g/cm^3 to about 0.935 g/cm^3, preferably from about 0.905 g/cm^3 to about 0.925 g/cm^3, and especially from about 0.905 g/cm^3 to less than about 0.92 g/cm^3.

The amount of the homogeneously branched linear or substantially linear ethylene/α-olefin polymer incorporated into the composition varies depending upon the heterogeneously branched ethylene polymer to which it is combined. However, about 50 percent (by weight of the total composition) of the homogeneous linear or substantially linear ethylene/α-olefin polymer is especially preferred in the novel compositions disclosed herein.

The molecular weight of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers for use in the present invention is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/2.16 kg (formerly known as "Condition (E)" and also known as I_2). Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. The lower melt index limit for the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers useful herein is generally about 0.001 grams/10 minutes (g/10 min). The upper melt index limit for the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers

is about 10 g/10 min, preferably less than about 1 g/10 min, and especially less than about 0.5 g/10 min.

Another measurement useful in characterizing the molecular weight of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/10 kg (formerly known as "Condition (N)" and also known as I_{10}). The ratio of the I_{10} and I_2 melt index terms is the melt flow ratio and is designated as I_{10}/I_2. Generally, the I_{10}/I_2 ratio for the homogeneously branched linear ethylene/α-olefin interpolymers is about 5.6. For the homogeneously branched substantially linear ethylene/α-olefin interpolymers used in the compositions of the invention, the I_{10}/I_2 ratio indicates the degree of long chain branching, i.e., the higher the I_{10}/I_2 ratio, the more long chain branching in the interpolymer. Generally, the I_{10}/I_2 ratio of the homogeneously branched substantially linear ethylene/α-olefin interpolymers is at least about 6, preferably at least about 7, especially at least about 8 or above. For the homogeneously branched substantially linear ethylene/α-olefin interpolymers, the higher the I_{10}/I_2 ratio, the better the processability.

Other additives such as antioxidants (e.g., hindered phenolics (e.g., Irganox® 1010 made by Ciba Geigy Corp.), phosphites (e.g., Irgafos® 168 also made by Ciba Geigy Corp.)), cling additives (e.g., PIB), antiblock additives, pigments, fillers, and the like can also be included in the formulations, to the extent that they do not interfere with the enhanced formulation properties discovered by Applicants.

Molecular Weight Distribution Determination

The molecular weight distribution of the linear or substantially linear olefin interpolymer product samples is analyzed by gel permeation chromatography (GPC) on a Waters 150C high temperature chromatographic unit equipped with three mixed porosity columns (Polymer Laboratories 10^3, 10^4, 10^5, and 10^6), operating at a system temperature of 140°C. The solvent is 1,2,4-trichlorobenzene, from which 0.3 percent by weight solutions of the samples are prepared

for injection. The flow rate is 1.0 milliliter/minute and the injection size is 200 microliters. A differential refractometer is being used as the detector.

The molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Word in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968, incorporated herein by reference) to derive the following equation:

$$M_{polyethylene} = a * (M_{polystyrene})^{b}.$$

In this equation, a = 0.4316 and b = 1.0. Weight average molecular weight, M_W, is calculated in the usual manner according to the following formula: $M_W = R\, w_i * M_i$, where w_i and M_i are the weight fraction and molecular weight, respectively, of the ith fraction eluting from the GPC column.

For both the homogeneously branched linear and substantially linear ethylene/α-olefin polymers, the molecular weight distribution (M_w/M_n) is preferably from about 1.8 to about 2.8, more preferably from about 1.89 to about 2.2 and especially about 2.

Determination of the Slope of Strain Hardening Coefficient

The slope of strain hardening is measured by compression molding a plaque from the polymer to be tested. Typically, the plaque is molded at about 177°C for 4 minutes under almost no pressure and then pressed for 3 minutes under a pressure of about 200 psi. The plaque is then allowed to cool at about 8°C/minute while still under 200 psi pressure. The molded plaque has a thickness of about 0.005 inches. The plaque is then cut into a dogbone shaped test piece using a steel rule die. The test piece is 0.315 inches wide and 1.063 inches long. The start of the curved portion of the dogbone shape begins at 0.315 inches from each

end of the sample and gently curves (i.e., tapers) to a width of 0.09 inches. The curve ends at a point 0.118 inches from the start of the curve such that the interior portion of the dogbone test piece has a width of 0.09 inches and a length of 0.197 inches.

The tensile properties of the test sample is tested on an Instron Tensile Tester at a crosshead speed of 1 inch/minute. The slope of strain hardening is calculated from the resulting tensile curve by drawing a line parallel to the strain hardening region of the resulting stress/strain curve. The strain hardening region occurs after the sample has pulled its initial load ((i.e., stress) usually with little or no elongation during the initial load) and after the sample has gone through a slight drawing stage (usually with little or no increase in load, but with increasing elongation (i.e., strain)). In the strain hardening region, the load and the elongation of the sample both continue to increase. The load increases in the strain hardening region at a much lower rate than during the initial load region and the elongation also increase, again at a rate lower than that experienced in the drawing region. Figure 1 shows the various stages of the stress/strain curve used to calculate the slope of strain hardening. The slope of the parallel line in the strain hardening region is then determined.

The slope of strain hardening coefficient (SHC) is calculated according to the following equation:

$$SHC = (\text{slope of strain hardening}) * (I_2)^{0.25}$$

where I_2 = melt index in grams/10 minutes.

For both the homogeneously branched linear and substantially linear ethylene/α-olefin interpolymers used in the invention, the SHC is greater than about 1.3, preferably greater than about 1.5.

Surprisingly, the slope of strain hardening coefficient reaches a maximum for the linear or the substantially linear ethylene/α-olefin polymers at a density from about 0.89 g/cm^3 to about 0.935 g/cm^3. Heterogeneous ethylene/α-olefin polymers, in contrast, do not behave in the same manner. Figure 1 graphically depicts the relationship between the density of the homogeneously branched substantially linear

ethylene polymers and ethylene/α-olefin polymers as a function of their slope of strain hardening coefficient, and includes a heterogeneously branched ethylene/1-octene copolymer (polymer W** in Table 1) for comparison purposes. Table 1 displays the data of Figure 1 in tabular form:

Table 1

Polymer	Melt Index (I_2) (g/10 min)	Density (g/cm^3)	I_{10}/I_2	SHC*
A	1	0.8564	7.36	0.004
B	1.03	0.8698	7.46	0.45
C	0.57	0.873	7.22	0.54
D	1.01	0.8817	7.36	0.89
E	1.06	0.9018	7.61	1.84
F	2.01	0.9041	8.07	2.03
G	0.77	0.9047	9.01	1.57
H	9.82	0.9048	7.03	1.67
I	4.78	0.9077	7.18	2.08
J	3.13	0.9113	7.67	2.04
K	2.86	0.9139	7.87	2.27
L	1.08	0.9197	8.07	2.24
M	0.96	0.9198	9.61	1.93
N	0.99	0.9203	9.09	2.23
O	1.11	0.9204	10.15	1.59
P	1.06	0.9205	9.08	2.25
Q	1.12	0.9216	8.94	2.3
R	30.74	0.9217	6.27	2
S	31.58	0.94	6.02	0.24
T	0.97	0.9512	12.11	0
U	0.97	0.9533	10.5	0
V	0.92	0.954	7.39	0
W**	0.8	0.905	8.7	1.02

*SHC = Slope of Strain Hardening Coefficient

**A comparative heterogeneously branched ethylene/1-octene copolymer

The Heterogeneously Branched Ethylene Polymer

The ethylene polymer to be combined with the homogeneous ethylene/α-olefin interpolymer is a heterogeneously branched (e.g., Ziegler polymerized) interpolymer of ethylene with at least one C_3-C_{20} α-olefin (e.g., linear low density polyethylene (LLDPE)).

Heterogeneously branched ethylene/α-olefin interpolymers differ from the homogeneously branched ethylene/α-olefin interpolymers primarily in their branching distribution. For example, heterogeneously branched LLDPE polymers have a distribution of branching, including a highly branched portion (similar to a very low density polyethylene), a medium branched portion (similar to a medium branched polyethylene) and an essentially linear portion (similar to linear homopolymer polyethylene). The amount of each of these fractions varies depending upon the whole polymer properties desired. For example, linear homopolymer polyethylene has neither branched nor highly branched fractions, but is linear. A very low density heterogeneous polyethylene having a density from about 0.9 g/cm^3 to about 0.915 g/cm^3 (such as Attane® copolymers, sold by The Dow Chemical Company and Flexomer® sold by Union Carbide Corporation) has a higher percentage of the highly short chain branched fraction, thus lowering the density of the whole polymer.

Heterogeneously branched LLDPE (such as Dowlex® sold by The Dow Chemical Company) has a lower amount of the highly branched fraction, but has a greater amount of the medium branched fraction. Figure 2 graphically depicts the relative amounts of these various fractions (as measured using temperature rising elution fractionation) for Dowlex® 2045 (a heterogeneously branched ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 min, a density of about 0.92 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 7.93 and a molecular weight distribution (M_W/M_n) of about 3.34), as compared with a homogeneously branched substantially linear ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 min, a density of about 0.92 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 10.5

and a molecular weight distribution (M_W/M_n) of about 2.18. Note that the homogeneously branched polymer has a single relatively narrow peak at an elution temperature of about 85°C, while the Dowlex® 2045 polymer has a broad branching distribution, as represented by the breadth of elution ~~temperatures~~ temperatures over which the polymer fractions elute. Dowlex® 2045 also has a distinct peak at an elution temperature of about 98°C, indicating the "linear" fraction of the whole polymer. Increasing the fraction of the polymer which has the beneficial properties, without ~~concommitantly~~ concomitantly increasing other fractions has not been demonstrated here-to-fore.

Preferably, however, the heterogeneously branched ethylene polymer is a heterogeneously branched Ziegler polymerized ethylene/α-olefin interpolymer having no more than about 10 percent (by weight of the polymer) of a polymer fraction having a SHC ≥ 1.3.

More preferably, the heterogeneously branched ethylene polymer is a copolymer of ethylene with a C_3-C_{20} α-olefin, wherein the copolymer has:

(i) a density from about 0.93 g/cm^3 to about 0.965 g/cm^3,

(ii) a melt index (I_2) from about 0.1 g/10 min to about 500 g/10 min, and

(iii) no more than about 10 percent (by weight of the polymer) of a polymer fraction having a SHC ≥ 1.3.

The heterogeneously branched ethylene/α-olefin interpolymers and/or copolymers also have at least two melting peaks as determined using Differential Scanning Calorimetry (DSC).

The Formulated Compositions

The compositions disclosed herein can be formed by any convenient method, including dry blending the individual components and subsequently melt mixing or by pre-melt mixing in a separate extruder (e.g., a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a twin screw extruder).

Another technique for making the compositions in-situ is disclosed in pending USSN 08/010,958, entitled Ethylene Interpolymerizations, which was filed January 29, 1993 in the names of Brian W.S. Kolthammer and Robert S. Cardwell, the disclosure of which is incorporated herein in its entirety by reference. USSN 08/010,958 describes, inter alia, interpolymerizations of ethylene and C_3-C_{20} alpha-olefins using a homogeneous catalyst in at least one reactor and a heterogeneous catalyst in at least one other reactor. The reactors can be operated sequentially or in parallel.

The compositions can also be made by fractionating a heterogeneous ethylene/α-olefin polymer into specific polymer fractions with each fraction having a narrow composition (i.e., branching) distribution, selecting the fraction having the specified properties (e.g., SHC ≥ 1.3), and blending the selected fraction in the appropriate amounts with another ethylene polymer. This method is obviously not as economical as the in-situ interpolymerizations of USSN 08/010,958, but can be used to obtain the compositions of the invention.

Fabricated Articles Made from the Novel Compositions

Many useful fabricated articles benefit from the novel compositions disclosed herein. For example, molding operations can be used to form useful fabricated articles or parts from the compositions disclosed herein, including various injection molding processes (e.g., that described in Modern Plastics Encyclopedia/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 264-268, "Introduction to Injection Molding" by H. Randall Parker and on pp. 270-271, "Injection Molding Thermoplastics" by Michael W. Green, the disclosures of which are incorporated herein by reference) and blow molding processes (e.g., that described in Modern Plastics Encyclopedia/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 217-218, "Extrusion-Blow Molding" by Christopher Irwin, the disclosure of which is incorporated herein by reference), profile extrusion, calandering, pultrusion (e.g., pipes) and the like. Rotomolded articles can also benefit from the novel compositions

described herein. Rotomolding techniques are well known to those skilled in the art and include, for example, those described in Modern Plastics Encyclopedia/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 296-301, "Rotational Molding" by R.L. Fair, the disclosure of which is incorporated herein by reference).

Fibers (e.g., staple fibers, melt blown fibers or spunbonded fibers (using, e.g., systems as disclosed in USP 4,340,563, USP 4,663,220, USP 4,668,566, or USP 4,322,027, all of which are incorporated herein by reference), and gel spun fibers (e.g., the system disclosed in USP 4,413,110, incorporated herein by reference)), both woven and nonwoven fabrics (e.g., spunlaced fabrics disclosed in USP 3,485,706, incorporated herein by reference) or structures made from such fibers (including, e.g., blends of these fibers with other fibers, e.g., PET or cotton)) can also be made from the novel compositions disclosed herein.

Film and film structures particularly benefit from the novel compositions described herein and can be made using conventional hot blown film fabrication techniques or other biaxial orientation processes such as tenter frames or double bubble processes. Conventional hot blown film processes are described, for example, in The Encyclopedia of Chemical Technology, Kirk-Othmer, Third Edition, John Wiley & Sons, New York, 1981, Vol. 16, pp. 416-417 and Vol. 18, pp. 191-192, the disclosures of which are incorporated herein by reference. Biaxial orientation film manufacturing process such as described in a "double bubble"process as in U.S. Patent 3,456,044 (Pahlke), and the processes described in U.S. Patent 4,352,849 (Mueller), U.S. Patent 4,597,920 (Golike), U.S. Patent 4,820,557 (Warren), U.S. Patent 4,837,084 (Warren), U.S. Patent 4,865,902 (Golike et al.), U.S. Patent 4,927,708 (Herran et al.), U.S. Patent 4,952,451 (Mueller), U.S. Patent 4,963,419 (Lustig et al.), and U.S. Patent 5,059,481 (Lustig et al.), the disclosures of each of which are incorporated herein by reference, can also be used to make film structures from the novel compositions described herein. The film structures can also be made as described in a tenter-frame technique, such as that used for oriented polypropylene.

Other multi-layer film manufacturing techniques for food packaging applications are described in Packaging Foods With Plastics, by Wilmer A. Jenkins and James P. Harrington (1991), pp. 19-27, and in "Coextrusion Basics" by Thomas I. Butler, Film Extrusion Manual: Process, Materials, Properties pp. 31-80 (published by TAPPI Press (1992)) the disclosures of which are incorporated herein by reference.

The films may be monolayer or multilayer films. The film made from the novel compositions can also be coextruded with the other layer(s) or the film can be laminated onto another layer(s) in a secondary operation, such as that described in Packaging Foods With Plastics, by Wilmer A. Jenkins and James P. Harrington (1991) or that described in "Coextrusion For Barrier Packaging" by W.J. Schrenk and C.R. Finch, Society of Plastics Engineers RETEC Proceedings, June 15-17 (1981), pp. 211-229, the disclosure of which is incorporated herein by reference. If a monolayer film is produced via tubular film (i.e., blown film techniques) or flat die (i.e., cast film) as described by K.R. Osborn and W.A. Jenkins in "Plastic Films, Technology and Packaging Applications" (Technomic Publishing Co., Inc. (1992)), the disclosure of which is incorporated herein by reference, then the film must go through an additional post-extrusion step of adhesive or extrusion lamination to other packaging material layers to form a multilayer structure. If the film is a coextrusion of two or more layers (also described by Osborn and Jenkins), the film may still be laminated to additional layers of packaging materials, depending on the other physical requirements of the final film. "Laminations Vs. Coextrusion" by D. Dumbleton (Converting Magazine (September 1992), the disclosure of which is incorporated herein by reference, also discusses lamination versus coextrusion. Monolayer and coextruded films can also go through other post extrusion techniques, such as a biaxial orientation process.

Extrusion coating is yet another technique for producing multilayer film structures using the novel compositions described herein. The novel compositions comprise at least one layer of the film structure. Similar to cast film, extrusion coating is a flat die technique.

A sealant can be extrusion coated onto a substrate either in the form of a monolayer or a coextruded extrudate.

Generally for a multilayer film structure, the novel compositions described herein comprise at least one layer of the total multilayer film structure. Other layers of the multilayer structure include but are not limited to barrier layers, and/or tie layers, and/or structural layers. Various materials can be used for these layers, with some of them being used as more than one layer in the same film structure. Some of these materials include: foil, nylon, ethylene/vinyl alcohol (EVOH) copolymers, polyvinylidene chloride (PVDC), polyethylene terephthalate (PET), oriented polypropylene (OPP), ethylene/vinyl acetate (EVA) copolymers, ethylene/acrylic acid (EAA) copolymers, ethylene/methacrylic acid (EMAA) copolymers, LLDPE, HDPE, LDPE, nylon, graft adhesive polymers (e.g., maleic anhydride grafted polyethylene), and paper. Generally, the multilayer film structures comprise from 2 to about 7 layers.

Example 1

Seventy five percent (by weight of the total composition) of a homogeneously branched substantially linear ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.91 g/cm^3, I_{10}/I_2 of about 10, M_w/M_n of about 2, and SHC of about 1.81 is dry blended and then melt blended with 25 percent (by weight of the total composition) of a heterogeneously branched ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.935 g/cm^3, I_{10}/I_2 of about 7.8, and M_w/M_n of about 3.4. The heterogeneously branched ethylene/1-octene copolymer has a fraction of about 5 percent (by weight of the heterogeneously branched copolymer) having a SHC ≥ 1.3. The dry blend is tumble blended in a 50 gallon drum for about 1 hour.

The melt blend is produced in a ZSK 30 twin screw extruder (30 mm screw diameter) and is then fabricated into film. The final blended composition has a density of about 0.919 g/cm^3.

The blended composition is then fabricated into blown film having a thickness of about 1 mil on an Egan Blown Film Line having a 2 inch diameter screw, a 3 inch die and at a 2.5 inch blow up ratio (BUR), as described in Table 2. For all film samples in Examples 1, 2, 4, and 6 and for comparative examples 3, 5, and 7, the targeted gauge is about 1 mil, using a blow-up ratio (BUR) of 2.5:1, a LLDPE screw design is used, a die gap of 70 mils is used, and a lay flat of about 11.875 inches is used.

Film properties are measured and reported in Table 3 with other examples of the invention and with comparative examples. Dart impact (type A) of the films is measured in accordance with ASTM D-1709-85; tensile strength, yield, toughness, and 2% secant modulus of the films is measured in accordance with ASTM D-882; Elmendorf tear (type B) is measured in accordance with ASTM D-1922; PPT tear is measured in accordance with ASTM D-2582; Block is measured in accordance with ASTM D-3354.

Puncture is measured by using an Instron tensiometer Tensile Tester with an integrator, a specimen holder that holds the film sample taut across a circular opening, and a rod-like puncturing device with a rounded tip (ball) which is attached to the cross-head of the Instron and impinges perpendicularly onto the film sample. The Instron is set to obtain a crosshead speed of 10 inches/minute and a chart speed (if used) of 10 inches/minute. Load range of 50% of the load cell capacity (100 lb. load for these tests) should be used. The puncturing device is installed to the Instron such that the clamping unit is attached to the lower mount and the ball is attached to the upper mount on the crosshead. Six film specimens are used (each 6 inches square). The specimen is clamped in the film holder and the film holder is secured to the mounting bracket. The crosshead travel is set and continues until the specimen breaks. Puncture resistance is defined as the energy to puncture divided by the volume of the film under test. Puncture resistance (PR) is calculated as follows:

$$PR = E/((12)(T)(A))$$

where PR = puncture resistance (ft-lbs/in^3)

E = energy (inch-lbs) = area under the load displacement curve

12 = inches/foot

T = film thickness (inches), and

A = area of the film sample in the clamp = 12.56 in^2.

Example 2

Seventy five percent (by weight of the total composition) of a homogeneously branched substantially linear ethylene/1-octene copolymer having I_2 of about 0.5 g/10 min, density of about 0.915 g/cm^3, I_{10}/I_2 of about 11, M_w/M_n of about 2.4, and SHC of about 2.265 is dry blended and then melt blended (as described in Example 1) with 25 percent (by weight of the total composition) of a heterogeneously branched ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.935 g/cm^3, I_{10}/I_2 of about 7.8, and M_w/M_n of about 3.4. The heterogeneously branched ethylene/1-octene copolymer has a fraction of about 5 percent (by weight of the heterogeneously branched copolymer) having a SHC ≥ 1.3. The final blended composition has a density of about 0.92 g/cm^3.

Blown film is made as described in Table 2 and film properties are measured and reported in Table 3 with other examples of the invention and with comparative examples.

Comparative Example 3

A heterogeneously branched ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.92 g/cm^3, I_{10}/I_2 of about 7.93, and M_w/M_n of about 3.34 is made into film as described in Example 1. The heterogeneously branched ethylene/1-octene copolymer has a fraction of about 36 percent (by weight of the heterogeneous copolymer) having a SHC ≥ 1.3. The entire heterogeneous ethylene/1-octene copolymer has a SHC of about 1.5.

Blown film is made as described in Table 2 and film properties are measured and reported in Table 3 with other examples of the invention and with comparative examples.

Example 4

Example 4 is an *in-situ* blend made according to USSN 08/010,958, wherein the homogeneously branched substantially linear polymer is made in a first reactor and is an ethylene/1-octene copolymer having a melt index (I_2) of about 0.5 g/10 min., and a density of about 0.9054 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 8.27 and a molecular weight distribution (M_W/M_n) of about 1.979 and comprises about 50% (by weight of the total composition). A heterogeneously branched ethylene/1-octene copolymer is made in a second reactor operated sequentially with the first reactor and has a melt index (I_2) of about 1.5 g/10 min., and a density of about 0.944 g/cm^3 and comprises the remaining 50% (by weight of the total composition). The total composition has a melt index (I_2) of about 1 g/10 min., a density of about 0.9248 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 7.22 and a molecular weight distribution (M_W/M_n) of about 2.641. This composition is made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

Comparative Example 5

Comparative Example 5 is an ethylene/1-octene copolymer made according to USSN 07/773,375, filed October 7, 1991, the disclosure of which is incorporated herein by reference. About 15% (by weight of the total composition) is made in a first reactor, with the remaining portion of the composition polymerized in a second sequentially operated reactor. Both reactors utilize Ziegler type catalysts and make heterogeneously branched polymers. The total composition has a melt index (I_2) of about 0.56 g/10 min., a density of about 0.9256 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 9.5 and a molecular weight distribution (M_W/M_n) of about 4.35. This composition is also made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

Example 6

Example 6 is an *in-situ* blend made according to USSN 08/010,958, wherein the homogeneously branched substantially linear polymer is made in a first reactor and is an ethylene/1-octene copolymer having a fractional melt index (I_2) , a density of about 0.906 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 8-10 and a molecular weight distribution (M_w/M_n) of about 2.2 and comprises about 43% (by weight of the total composition). A second heterogeneously branched ethylene/1-octene copolymer is made in a second ~~reeator~~ reactor operated sequentially with the first reactor and has a melt index (I_2) of about 0.85 g/10 minutes, a density of about 0.938 g/cm^3 and comprises the remaining 57% (by weight of the total composition). The total composition has a melt index (I_2) of about 0.53 g/10 minutes, a density of about 0.9246 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 7.83, and a molecular weight distribution (M_w/M_n) of about 2.8. This composition is made into blown film as described in Table 2 and the film properties are reported in Table 3.

Comparative Example 7

Comparative Example 7 is an ethylene/1-octene copolymer made according to USSN 07/773,375, filed October 7, 1991, the disclosure of which is incorporated herein by reference. About 25% (by weight of the total composition) is made in a first reactor, with the remaining portion of the composition polymerized in a second sequentially operated reactor. Both reactors utilize Ziegler type catalysts and make heterogeneously branched polymers. The total composition has a melt index (I_2) of about 0.49 g/10 min., a density of about 0.9244 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 10 and a molecular weight distribution (M_w/M_n) of about 4.78. This composition is also made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

Comparative Example 8

Comparative example 8 is a heterogeneously branched ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 minutes, a density of ~~baout~~ about 0.9249 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 8 and a molecular weight ~~distrubution~~ distribution (M_W/M_n) of about 3.5.

Blown film is made as described in Table 2 and film properties are measured and reported in Table 3 with other examples of the invention and comparative examples.

Table 2

	Ex. 1	Ex. 2	Comp. Ex. 3	Ex. 4	Comp. Ex. 5	Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Zone 1A (°F)	300	300	300	300	300	300	300	300
Zone 1B (°F)	450	451	475	474	475	475	475	474
Zone 1C (°F)	450	450	475	475	475	475	475	475
Zone 2A (°F)	450	450	475	474	475	475	475	475
Zone 2B (°F)	450	450	455	475	475	475	475	475
Zone 2C (°F)	450	450	475	475	475	475	475	475
Zone 3 (°F)	451	452	474	477	477	476	476	474
Zone 4 (°F)	450	450	473	475	475	475	475	475
Zone 5 (°F)	450	450	475	475	475	475	475	475
Melt temp. (°F)	475	477	515	501	502	499	499	497
Blower Air temp. (°F)	47.3	45.7	57	44.4	86.5	47.6	NA	47.3
Chill Water temp. (°F)	39	37.6	51.1	38.3	86.8	40	38.7	40.5
Extruder Die press. (psi)	2843	3427	1321	1874	1763	2883	2525	1952
Nozzle press. (in.)	3.2	4.5	4.38	4.4	4.9	4.6	4.6	4.3
Amps	27.3	33.1	37.7	39.9	40.2	50.1	42.6	38.6
Extruder speed (rpm)	27.6	28.8	21.5	23.1	21.1	21.5	22.1	21.7
Nip Roll speed (rpm)	33.1	36.9	39	39.8	36.2	37	36	37.8
Output (lbs/hr)	31	NR*	38.3	39	NR*	36	36	36
Frost line height (in.)	12.5	9	13	12	12	10.5	11	10.5

*NR = Not recorded

Table 3

	Ex. 1	Ex. 2	Comp. Ex. 3	Ex. 4	Comp. Ex. 5	Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Yield (MD*) (psi)	1605	1595	1643	2040	2243	1973	1810	1782
Tensile (MD*) (psi)	8522	9525	7444	7794	7931	9325	8455	4928
Toughness (MD*) ($ft\text{-}lbs/in^3$)	1689	1773	1439	1671	1519	NR	NR	~~549~~ NR
Yield (CD**) (psi)	1530	1489	1706	2267	2407	1997	1809	1832
Tensile (CD**) (psi)	6252	7603	5807	7079	7458	7153	6326	4598
Toughness (CD**) ($ft\text{-}lbs/in^3$)	1282	1599	1358	1656	1495	NR	NR	~~507~~ NR
Elmendorf B (MD*) (grams)	288	216	334	317	194	320	398	~~438~~ 297
Elmendorf B (CD**) (grams)	621	566	413	630	664	640	621	~~550~~ 527
PPT Tear (MD*) (lbs.)	6.79	6.18	5.99	6.2	6.5	6.2	6.2	~~5.3~~ 5.8
PPT Tear (CD**) (lbs.)	7.44	7.42	6.46	6.8	8.1	7.0	7.5	~~6.3~~ 6.7
Dart Impact A (grams)	708	610	354	410	186	412	186	164
Puncture ($ft\text{-}lbs/in^3$)	316	349	251	231	256	250	227	237
Film Block g.	75	33	87	32	17	11.8	17	22
Film Gradient Density (g/cm^3)	0.9145	0.9153	0.9155	0.9205	0.9218	0.9198	0.9201	0.9206
Film Gauge (low) (mils)	0.9	0.9	0.9	0.85	0.8	0.98	0.95	1.05
Film Gauge (high) (mils)	1.2	1.05	1.1	0.95	1	1.08	1.05	1.15

*MD = Machine direction

**CD = Cross direction

NR = Not Recorded

In general, films made from the novel formulated ethylene/α-olefin compositions exhibit good impact and tensile properties, and an especially good combination of tensile, yield and toughness (e.g., toughness and dart impact). Further, films from the example resins exhibited significant improvements over films made from the comparative resins in a number of key properties.

For example, comparing examples 1 and 2 with comparative example 3, the data show films produced from the melt blends (examples 1 and 2) exhibited significantly higher values for the following film properties: dart ~~ipact~~ impact, MD tensile, CD tensile, MD toughness, CD toughness MD ppt tear, ~~DC~~ CD ppt tear, CD Elmendorf tear B, puncture and significantly lower block.

Comparing example 4 to comparative example 5, the data show films produced from the *in-situ* blend (made according to USSN 08/010,958) exhibited significantly higher values for the following film properties: dart impact, MD toughness and CD toughness.

Comparing example 6 to comparative examples 7 (an ethylene/1-octene copolymer made according to USSN 07/773,375) and 8 (an heterogeneously branched ethylene/1-octene copolymer), the data show films produced from the *in-situ* blend (made according to USSN 08/010,958) exhibited significantly higher values for the following film properties: dart impact, MD yield, CD yield, MD tensile, CD tensile, CD Elmendorf tear B and puncture and significantly lower block.

We Claim:

1. A film made from an ethylene polymer composition, wherein the composition comprises from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of :

(A) at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_W/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min) to about 10 g/10 min,

(iv) no linear polymer fraction, and

(v) a single melting peak as measured using differential scanning calorimetry; and

(B) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one heterogeneously branched ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3.

2. The film of claim 1 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer has a slope of strain hardening coefficient greater than or equal to about 1.3.

3. The film of claim 1 wherein the heterogeneously branched ethylene polymer is an interpolymer of ethylene with at least one C_3-C_{20} α-olefin.

4. The film of claim 1 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer is an interpolymer of ethylene with at least one C_3-C_{20} α-olefin.

5. The film of claim 1 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer is a copolymer of ethylene and a C_3-C_{20} α-olefin.

6. The film of claim 5 wherein the homogeneously branched substantially linear ethylene/α-olefin copolymer is a copolymer of ethylene and 1-octene.

7. The film of claim 3 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and a C_3-C_{20} α-olefin.

8. The film of claim 7 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and 1-octene.

9. A film made from an ethylene polymer composition, wherein the composition comprises from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of :

(A) at least one homogeneously branched linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_W/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min) to about 10 g/10 min,

(iv) no linear polymer fraction, and

(v) a single melting peak as measured using differential scanning calorimetry; and

(B) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one heterogeneously branched ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3.

10. The film of claim 9 wherein the homogeneously branched linear ethylene polymer has a slope of strain hardening coefficient greater than or equal to about 1.3.

11. The film of claim 9 wherein the heterogeneously branched ethylene polymer is an interpolymer of ethylene with at least one C_3-C_{20} α-olefin.

12. The film of claim 9 wherein the homogeneously branched linear ethylene/α-olefin interpolymer is an interpolymer of ethylene with at least one C_3-C_{20} α-olefin.

13. The film of claim 9 wherein the homogeneously branched linear ethylene/α-olefin interpolymer is a copolymer of ethylene and a C_3-C_{20} α-olefin.

14. The film of claim 13 wherein the homogeneously branched linear ethylene/α-olefin copolymer is a copolymer of ethylene and 1-octene.

15. The film of claim 11 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and a C_3-C_{20} α-olefin.

16. The film of claim 15 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and 1-octene.

17. In a composition comprising at least one homogeneously branched ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene/α-olefin interpolymer, the improvement comprising incorporating into the composition from about 10 percent (by weight of the total composition) to about 95 percent

(by weight of the total composition) of at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_W/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min) to about 10 g/10 min,

(iv) no linear polymer fraction, and

(v) a single melting peak as measured using differential scanning calorimetry.

18. The improvement of claim 17 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer has a slope of strain hardening coefficient greater than or equal to about 1.3.

19. The improvement of claim 17 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer is an interpolymer of ethylene with at least one C_3-C_{20} α-olefin.

20. The improvement of claim 17 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer is a copolymer of ethylene and a C_3-C_{20} α-olefin.

21. The improvement of claim 20 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer is a copolymer of ethylene and 1-octene.

22. The improvement of claim 17 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and a C_3-C_{20} α-olefin.

23. The improvement of claim 22 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and 1-octene.

24. In a composition comprising at least one homogeneously branched ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene/α-olefin interpolymer, the improvement comprising incorporating into the composition from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one homogeneously branched linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min) to about 10 g/10 min,

(iv) no linear polymer fraction, and

(v) a single melting peak as measured using differential scanning calorimetry.

25. The improvement of claim 24 wherein the homogeneously branched linear ethylene/α-olefin interpolymer has a slope of strain hardening coefficient greater than or equal to about 1.3.

26. The improvement of claim 24 wherein the homogeneously branched linear ethylene/α-olefin interpolymer is an interpolymer of ethylene with at least one C_3-C_{20} α-olefin.

27. The improvement of claim 24 wherein the homogeneously branched linear ethylene/α-olefin interpolymer is a copolymer of ethylene and a C_3-C_{20} α-olefin.

28. The improvement of claim 27 wherein the homogeneously branched linear ethylene/α-olefin interpolymer is a copolymer of ethylene and 1-octene.

29. The improvement of claim 24 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and a C_3-C_{20} α-olefin.

30. The improvement of claim 29 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and 1-octene.

Abstract of the Disclosure

Fabricated articles made from formulated ethylene polymer compositions are disclosed. Films made from such formulated compositions have surprisingly good impact and tensile properties, and an especially good combination of modulus and toughness. The ethylene polymer compositions have at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene polymer. The homogeneously branched substantially linear ethylene/α-olefin interpolymer has a density from about 0.89 to about 0.92 g/cm^3 and a slope of strain hardening coefficient greater than or equal to about 1.3.

This Declaration and Power of Attorney 1000 is in the ENGLISH language and has the same meaning in other languages with the same 1000 number

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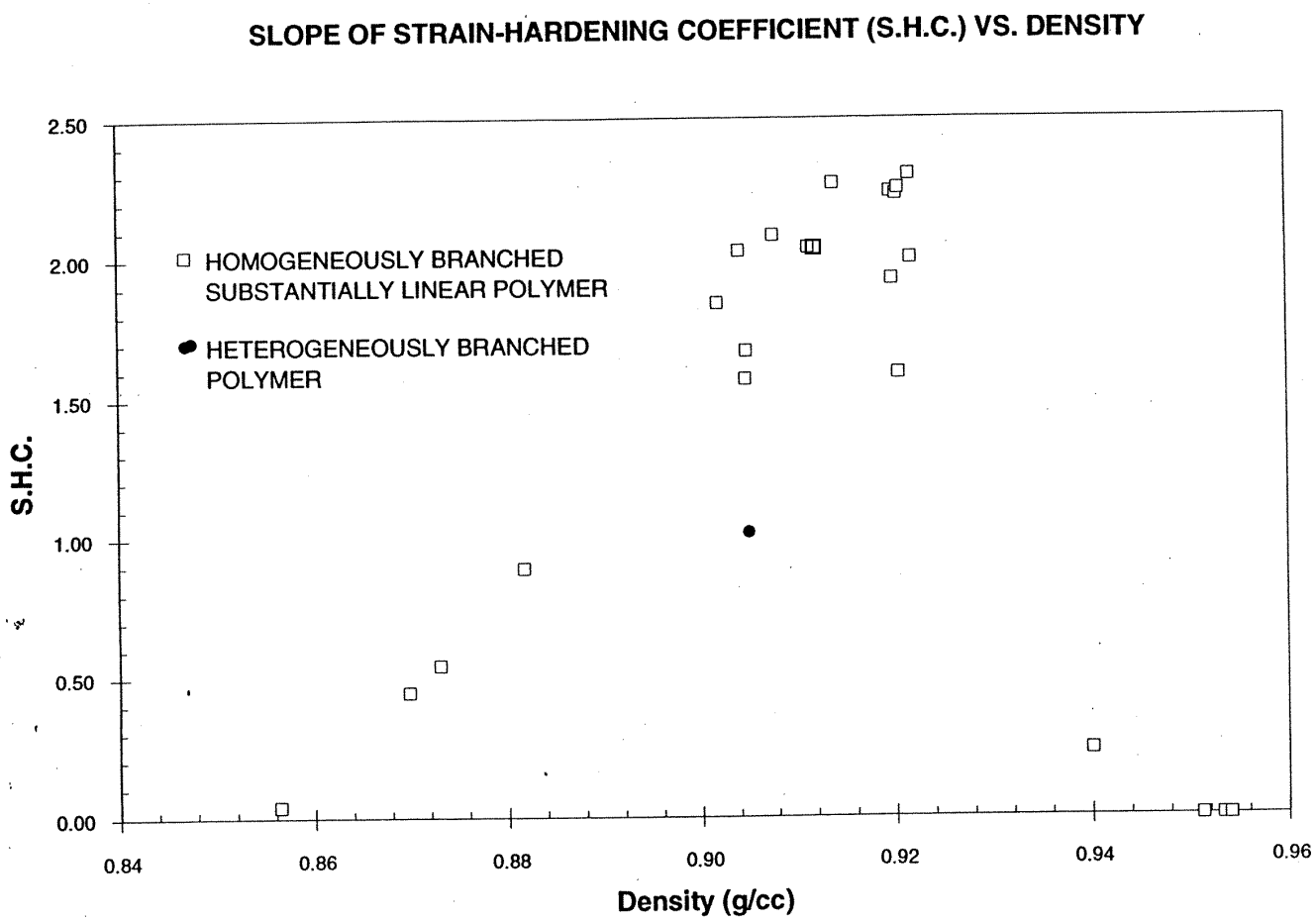
FIGURE 1

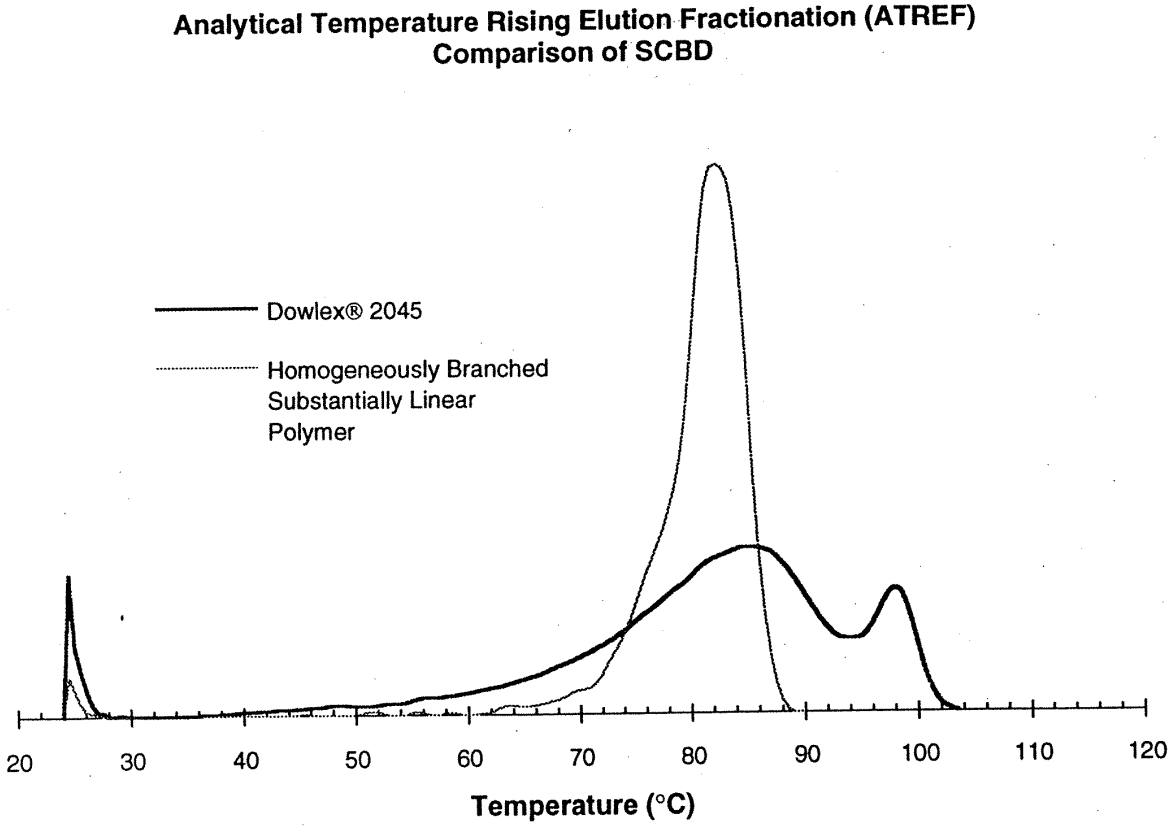
08/054379



PRINT OF DRAWINGS AS ORIGINALLY FILED

08/054379

Figure 2



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UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office
Address: COMMISSIONER OF PATENTS AND TRADEMARKS
Washington, D.C. 20231

APPLICATION NUMBER	FILING DATE	FIRST NAMED APPLICANT		ATTY. DOCKET NO./TITLE
08/054,379	04/28/93	CHUM	P	C401210

0351/0621

THE DOW CHEMICAL CO.
PATENT DEPARTMENT
B.LDG. B-1211
DALLAS, TX 77541 0000

DATE MAILED: 06/21/93

NOTICE TO FILE MISSING PARTS OF APPLICATION FILING DATE GRANTED

An Application Number and Filing Date have been assigned to this application. However, the items indicated below are missing. The required items and fees identified below must be timely submitted **ALONG WITH THE PAYMENT OF A SURCHARGE** for items 1 and 3-6 only of $130.00 for large entities or $65.00 for small entities who have filed a verified statement claiming such status. The surcharge is set forth in 37 CFR 1.16(e).

If all required items on this form are filed within the period set below, the total amount owed by applicant as a ~~☐ large~~ entity, ☐ small entity (verified statement filed), is $130.00

Applicant is given **ONE MONTH FROM THE DATE OF THIS LETTER, OR TWO MONTHS FROM THE FILING DATE** of this application, **WHICHEVER IS LATER,** within which to file all required items and pay any fees required above to avoid abandonment. Extensions of time may be obtained by filing a petition accompanied by the extension fee under the provisions of 37 CFR 1.136(a).

1. ☐ The statutory basic filing fee is: ☐ missing ☐ insufficient. Applicant as a ☐ large entity ☐ small entity, must submit $_____ to complete the basic filing fee.

2. ☐ Additional claim fees of $_____ as a ☐ large entity, ☐ small entity, including any required multiple dependent claim fee, are required. Applicant must submit the additional claim fees or cancel the additional claims for which fees are due.

3. ☐ The oath or declaration:
   ☐ is missing.
   ☐ does not cover items omitted at time of execution.

   An oath or declaration in compliance with 37 CFR 1.63, identifying the application by the above Application Number and Filing Date is required.

4. ☐ The oath or declaration does not identify the application to which it applies. An oath or declaration in compliance with 37 CFR 1.63, identifying the application by the above Application Number and Filing Date, is required.

5. ☑ The signature to the oath or declaration is: ☑ missing; ☐ a reproduction; ☐ by a person other than the inventor or a person qualified under 37 CFR 1.42, 1.43, or 1.47. A properly signed oath or declaration in compliance with 37 CFR 1.63, identifying the application by the above Application Number and Filing Date, is required.

6. ☐ The signature of the following joint inventor(s) is missing from the oath or declaration:

   _____. An oath or declaration listing the names of all inventors and signed by the omitted inventor(s), identifying this application by the above Application Number and Filing Date, is required.

7. ☐ The application was filed in a language other than English. Applicant must file a verified English translation of the application and a fee of $_____ under 37 CFR 1.17(k), unless this fee has already been paid.

8. ☐ A $_____ processing fee is required for returned checks. (37 CFR 1.21(m)).

9. ☐ Your filing receipt was mailed in error because check was returned without payment.

10. ☐ The application does not comply with the Sequence Rules. See attached Notice to Comply with Sequence Rules 37 CFR 1.821-1.825.

11. ☐ Other.

~~Direct the response and any questions about this notice to~~ _____, Application Processing Division, Special Processing and Correspondence Branch (703) 308-1202.

A copy of this notice MUST be returned with the response.

FORM PTO-1533 (REV. 1-93) **OFFICE COPY**



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Pak-Wing Steve Chum
Serial No.: 08/054379 Group Art Unit:
Filed: April 28, 1993 Examiner:
For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

RECEIVED
AUG 0 5 1993
APPLICATION DIVISION

I HEREBY CERTIFY THAT THIS CORRESPONDENCE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE AS FIRST CLASS MAIL IN AN ENVELOPE ADDRESSED TO: COMMISSIONER OF PATENTS AND TRADEMARKS, WASHINGTON, D.C. 20231, On July 7, 1993
DATE OF DEPOSIT
Margaret Greene
PRINT OR TYPE NAME OF PERSON SIGNING CERTIFICATE
Margaret Greene
SIGNATURE OF PERSON SIGNING CERTIFICATE
July 7, 1993
DATE OF SIGNATURE

Hon. Commissioner of Patents & Trademarks
Washington, D.C. 20231

Sir:

FILING OF DECLARATION

Filed herewith is the Declaration and Power of Attorney in the above-identified patent application. The filing date of the application is as noted above.

The $130.00 fee for the separate filing of this Declaration required under 37 CFR 1.16(e) may be charged to our Deposit Account No. 04-1512. Duplicate copies of this sheet are enclosed.

Respectfully submitted,

By L. Wayne White

L. Wayne White
Registration No. 25,415
Phone: 409-238-2149

Freeport, Texas 77541
LWW/mfg

C-40,121-G -1-

This Declaration and Power of Attorney 1000 is in the ENGLISH language and has the same meaning in other languages with the same 1000 number.

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#3 A/N





UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office
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Washington, D.C. 20231

APPLICATION NUMBER	FILING DATE	FIRST NAMED APPLICANT		ATTY. DOCKET NO./TITLE
08/054,379	04/28/93	CHUM	P	C401216

03B1/0621

THE DOW CHEMICAL CO.
PATENT DEPARTMENT
BLDG. B-1211
DALLAS, TX 77541

0000

DATE MAILED: 06/21/93

NOTICE TO FILE MISSING PARTS OF APPLICATION FILING DATE GRANTED

An Application Number and Filing Date have been assigned to this application. However, the items indicated below are missing. The required items and fees identified below must be timely submitted **ALONG WITH THE PAYMENT OF A SURCHARGE** for items 1 and 3-6 only of $130.00 for large entities or $65.00 for small entities who have filed a verified statement claiming such status. The surcharge is set forth in 37 CFR 1.16(e).

If all required items on this form are filed within the period set below, the total amount owed by applicant as a ~~☐ large~~ entity, ☐ small entity (verified statement filed), is $130.00

Applicant is given **ONE MONTH FROM THE DATE OF THIS LETTER, OR TWO MONTHS FROM THE FILING DATE** of this application, **WHICHEVER IS LATER,** within which to file all required items and pay any fees required above to avoid abandonment. Extensions of time may be obtained by filing a petition accompanied by the extension fee under the provisions of 37 CFR 1.136(a).

1. ☐ The statutory basic filing fee is: ☐ missing ☐ insufficient. Applicant as a ☐ large entity ☐ small entity, must submit $_____ to complete the basic filing fee.

2. ☐ Additional claim fees of $_____ as a ☐ large entity, ☐ small entity, including any required multiple dependent claim fee, are required. Applicant must submit the additional claim fees or cancel the additional claims for which fees are due.

3. ☐ The oath or declaration:
   ☒ is missing.
   ☐ does not cover items omitted at time of execution.

   An oath or declaration in compliance with 37 CFR 1.63, identifying the application by the above Application Number and Filing Date is required.

4. ☐ The oath or declaration does not identify the application to which it applies. An oath or declaration in compliance with 37 CFR 1.63, identifying the application by the above Application Number and Filing Date, is required.

5. ☑ The signature to the oath or declaration ~~is~~ are ☒ missing; ☐ a reproduction; ☐ by a person other than the inventor or a person qualified under 37 CFR 1.42, 1.43, or 1.47. A properly signed oath or declaration in compliance with 37 CFR 1.63, identifying the application by the above Application Number and Filing Date, is required.

6. ☐ The signature of the following joint inventor(s) is missing from the oath or declaration:

   _____. An oath or declaration listing the names of all inventors and signed by the omitted inventor(s), identifying this application by the above Application Number and Filing Date, is required.

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8. ☐ A $_____ processing fee is required for returned checks. (37 CFR 1.21(m)).

9. ☐ Your filing receipt was mailed in error because check was returned without payment.

10. ☐ The application does not comply with the Sequence Rules. See attached Notice to Comply with Sequence Rules 37 CFR 1.821-1.825.

11. ☐ Other.

~~Direct the response and any questions about this notice to~~ _____, Application Processing Division, Special Processing and Correspondence Branch (703) 308-1202.

SC13307 08/04/93 08054379 04-1512 130 105 130.00CH

A copy of this notice MUST be returned with the response.

FORM PTO-1533 (REV. 1-93) **COPY TO BE RETURNED WITH RESPONSE**

UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office
Address: COMMISSIONER OF PATENTS AND TRADEMARKS
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.
08/054,379	04/28/93	CHUM	P C401216

EXAMINER: WU, D

15M2/1115

ART UNIT	PAPER NUMBER
1505	4

THE DOW CHEMICAL CO.
PATENT DEPARTMENT
BLDG. B-1211
DALLAS, TX 77541

DATE MAILED: 11/15/93

This is a communication from the examiner in charge of your application.
COMMISSIONER OF PATENTS AND TRADEMARKS

☒ This application has been examined ☐ Responsive to communication filed on _____ ☐ This action is made final.

A shortened statutory period for response to this action is set to expire 3 month(s), _____ days from the date of this letter.
Failure to respond within the period for response will cause the application to become abandoned. 35 U.S.C. 133

Part I THE FOLLOWING ATTACHMENT(S) ARE PART OF THIS ACTION:

1. ☒ Notice of References Cited by Examiner, PTO-892.
2. ☐ Notice of Draftsman's Patent Drawing Review, PTO-948.
3. ☐ Notice of Art Cited by Applicant, PTO-1449.
4. ☐ Notice of Informal Patent Application, PTO-152.
5. ☐ Information on How to Effect Drawing Changes, PTO-1474.
6. ☐ _____.

Part II SUMMARY OF ACTION

1. ☒ Claims 1-30 are pending in the application.
   Of the above, claims 9-16, and 24-30 are withdrawn from consideration.
2. ☐ Claims _____ have been cancelled.
3. ☐ Claims _____ are allowed.
4. ☒ Claims 1-8, and 17-23 are rejected.
5. ☐ Claims _____ are objected to.
6. ☐ Claims _____ are subject to restriction or election requirement.
7. ☐ This application has been filed with informal drawings under 37 C.F.R. 1.85 which are acceptable for examination purposes.
8. ☐ Formal drawings are required in response to this Office action.
9. ☐ The corrected or substitute drawings have been received on _____. Under 37 C.F.R. 1.84 these drawings are ☐ acceptable; ☐ not acceptable (see explanation or Notice of Draftsman's Patent Drawing Review, PTO-948).
10. ☐ The proposed additional or substitute sheet(s) of drawings, filed on _____. has (have) been ☐ approved by the examiner; ☐ disapproved by the examiner (see explanation).
11. ☐ The proposed drawing correction, filed _____, has been ☐ approved; ■ disapproved (see explanation).
12. ☐ Acknowledgement is made of the claim for priority under 35 U.S.C. 119. The certified copy has ☐ been received ☐ not been received ☐ been filed in parent application, serial no. _____; filed on _____.
13. ☐ Since this application apppears to be in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under Ex parte Quayle, 1935 C.D. 11; 453 O.G. 213.
14. ☐ Other

EXAMINER'S ACTION

PTOL-326 (Rev. 2/93)

15. Restriction to one of the following inventions is required under 35 U.S.C. § 121:

I. Claims 1-8, and 17-23, drawn to an ethylene polymer film, classified in Class 525, subclass 240.

II. Claims 9-16, and 24-30, drawn to an ethylene polymer film, classified in Class 525, subclass 240.

16. The inventions are distinct, each from the other because of the following reasons:

Group I and Group II are related as mutually independent/exclusive inventions in view of the definition of "substantially linear ethylene/alpha-olefin interpolymer" and "linear ethylene/alpha-olefin interpolymer" defined in pages 4 and page 6 in the specification; the independent/exclusive inventions of Group I and Group II being also admitted by the applicants' attorney, Mr. Stephen Krupp in the telephone interview on November 9, 1993.

17. Because these inventions are distinct for the reasons given above and have acquired a separate status in the art because of their recognized divergent subject matter, restriction for examination purposes as indicated is proper.

18. During a telephone conversation with applicants' attorney, Mr. L. Wayne White and Mr. Stephen Krupp on November 9, 1993 a provisional election was made with traverse to prosecute the invention of Group I, claim 1-8, and 17-23. Affirmation of this election must be made by applicant in responding to this Office action. Claims 9-16, and 24-30 are withdrawn from further consideration by the Examiner, 37 C.F.R. § 1.142(b), as being drawn to a non-elected invention.

19. Applicant is reminded that upon the cancellation of claims to a non-elected invention, the inventorship must be amended in compliance with 37 C.F.R. § 1.48(b) if one or more of the currently named inventors is no longer an inventor of at least one claim remaining in the application. Any amendment of inventorship must be accompanied by a diligently-filed petition under 37 C.F.R. § 1.48(b) and by the fee required under 37 C.F.R. § 1.17(h).

20. Claims 1-8, and 17-23 are rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

21. In claim 1, line 5-6, "substantially linear ethylene/alpha-olefin interpolymer" being used as one of the ethylene polymers to make the claimed film; however, in line 13, "no linear polymer fraction" being described as one of the characteristics of said ethylene polymer. It appears that it contradicts to its own definition. The same confusion exists in the claim 17.

22. Claims 2 and 18 are rejected under 35 U.S.C. § 112, first paragraph, as the disclosure is enabling only for claims limited the strain hardening coefficient up to 2.265. See M.P.E.P. §§ 706.03(n) and 706.03(z).

23. The specification lacks guidance that would lead one skilled in the art to obtain the same working example results by using an ethylene interpolymer having a significantly higher SHC, such as 20. Therefore, it appears that one of ordinary skill in the art would be subjected to undue experimentation to do so. In other words, this rejection is based upon that applicants fail to provide an upper limit of the SHC of the ethylene interpolymer by using the term "greater than" in the claim. In re Fischer, 166 USPQ 18 (CCPA 1970).

24. The following is a quotation of the appropriate paragraphs of 35 U.S.C. § 102 that form the basis for the rejections under this section made in this Office action:

> A person shall be entitled to a patent unless --
> (b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

25. The following is a quotation of 35 U.S.C. § 103 which forms the basis for all obviousness rejections set forth in this Office action:

> A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.
>
> Subject matter developed by another person, which qualifies as prior art only under subsection (f) or (g) of section 102 of this title, shall not preclude patentability under this section where the subject matter and the claimed invention were, at the time the invention was made, owned by the same person or subject to an obligation of assignment to the same person.

26. Claims 1-8, and 17-23 are rejected under 35 U.S.C. § 102(b) as anticipated by or, in the alternative, under 35 U.S.C. § 103 as obvious over WO '414.

27. In examples 1 and 2, and Table 1, WO '414 discloses polymer blends B1 and B2 made by ethylene polymers '006, and '013

wherein the MWD, melt index, and density fall into the same ranges as claimed. Although WO '414 fails to show the value of the slope of strain hardening coefficient of polymer '013, in view of other substantially similar physical properties, the examiner has a reasonable basis to believe that it inherently possesses said slope of strain hardening coefficient, and the polymer blends of WO '414 are not necessarily different from the claimed polymer blends. Since the examiner does not have proper equipment to carry out the analytical tests, the burden is on the applicants to prove the claimed polymer blends are necessarily different from those of WO '414 and unobvious thereof. In re Fitzgerald et al. 205 USPQ 594.

28. Claims 1-8, and 17-23 are rejected under 35 U.S.C. § 103 as being unpatentable over Hodgson, Jr..

29. The issue date of Hodgson reference (4-27-93) is deemed good as 102(a) reference in view of the filing date of the instant application (4-28-93). Although the filing date of the parent application was 10-15-91, it should be noted that any added new subject matter does not receive benefit of the filing date of any earlier filed application, but that the repeated subject matter does.

30. Hodgson, Jr. discloses a polyolefin film material comprising a blend of an olefin polymer and an ethylene copolymer wherein the ethylene copolymer has all the claimed characteristics, such as density (0.88 to 0.915 g/cm3), melt index (0.5 to 7.5 dg/min.), MWD (1.5 to 3.5), and an essentially single melting point (See abstract, claim 1). In examples 5-6, and 9-10, the polyolefin films were made by the blends of said ethylene copolymer and either PEC or PP; however, at column 4, lines 14-26, and claims 8-10, PP, LDPE, LLDPE, PEC, and HDPE etc. are disclosed as species of said olefin polymer which generally exhibits a density in excess of about 0.915 g/cm3. Therefore, it would have been obvious to one person having ordinary skill in the art to use HDPE with a density higher than 0.93 g/cm3 rather than PEC or PP in the working examples since all the species of a genus would function equally well, motivated by reasonable expectation of success. In re O'Farrell, 7 USPQ 2d. 1673 (Fed. Cir. 1988).

31. Although Hodgson, Jr. fail to show the value of the slope of strain hardening coefficient of ethylene polymer, in view of other substantially similar physical properties, the examiner has a reasonable basis to suspect that it would possess said slope of strain hardening coefficient. Moreover, it has been held in the case law that the mere fact that the reference does not mention

the claimed property does not alone defeat a prima facie case of obviousness. In re Dillon, 16 USPQ 2D. 1897 (CAFC 1990)

30. Any inquiry concerning this communication or earlier communications from the examiner should be directed to David Wu whose telephone number is (703) 308-2450.

Joseph L. Schofer

JOSEPH L. SCHOFER
SUPERVISORY PATENT EXAMINER
ART UNIT 155

dw

David Wu
November 10, 1993

TO SEPARATE, [illegible] TOP AND BOTTOM EDGES, SNAP-APART AND DISCARD CARBON

FORM PTO-892 (REV. 3-78)	U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	SERIAL NO.	GROUP ART UNIT	ATTACHMENT TO PAPER NUMBER
NOTICE OF REFERENCES CITED		08/054,379	1505	4
		APPLICANT(S) CHUM ET AL		

U.S. PATENT DOCUMENTS

*		DOCUMENT NO.	DATE	NAME	CLASS	SUB-CLASS	FILING DATE IF APPROPRIATE
	A	5206075	4-93	Hodgson, Jr.	428	216	12-91
	B						
	C						
	D						
	E						
	F						
	G						
	H						
	I						
	J						
	K						

FOREIGN PATENT DOCUMENTS

*		DOCUMENT NO.	DATE	COUNTRY	NAME	CLASS	SUB-CLASS	PERTINENT SHTS. DWG	PERTINENT PP. SPEC.
	L	90/03414	4-90	PCT		—	—		
	M								
	N								
	O								
	P								
	Q								

OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)

	R	
	S	
	T	
	U	

EXAMINER	DATE
David Wu	11-10-93

* A copy of this reference is not being furnished with this office action.
(See Manual of Patent Examining Procedure, section 707.05 (a).)

US005206075A

United States Patent [19]

Hodgson, Jr.

[11] Patent Number: 5,206,075

[45] Date of Patent: Apr. 27, 1993

[54] **SEALABLE POLYOLEFIN FILMS CONTAINING VERY LOW DENSITY ETHYLENE COPOLYMERS**

[75] Inventor: **William J. Hodgson, Jr.**, Baytown, Tex.

[73] Assignee: **Exxon Chemical Patents Inc.**, Linden, N.J.

[21] Appl. No.: **810,473**

[22] Filed: **Dec. 19, 1991**

[51] **Int. Cl.**[5] **B32B 7/02**

[52] **U.S. Cl.** **428/216**; 428/349; 428/516; 428/500; 525/240

[58] **Field of Search** 428/516, 349, 500, 216; 525/240

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,291,092	9/1981	Weiner	428/349
4,643,945	2/1987	Kiang	428/349
4,764,404	8/1988	Genske et al.	428/35

FOREIGN PATENT DOCUMENTS

0221726	5/1987	European Pat. Off. .
0247897	12/1987	European Pat. Off. .
0341091	11/1989	European Pat. Off. .

Primary Examiner—Edith Buffalow
Attorney, Agent, or Firm—Jaimes Sher

[57] **ABSTRACT**

The invention provides laminar polyolefin film materials having a base film layer comprising a blend of an olefin polymer and up to about 30% by weight of at least one very low density copolymer of ethylene and a C_3 to C_{20} alpha olefin comonomer copolymerizable with ethylene, said base layer having a heat sealable film layer present on one or both surfaces thereof comprising a very low density copolymer of ethylene and a copolymerizable C_5 to C_{12} alpha olefin comonomer. The ethylene copolymer constituents of the film are characterized as having a density in the range of about 0.88 g/cm^3 to abut 0.915 g/cm^3, a melt index in the range of about 0.5 dg/min to about 7.5 dg/min, a molecular weight distribution (M_w/M_n) of about 1.5 to about 3.5 and an essentially single melting point in the range of about 60° C. to about 115° C., measured as a DSC peak T_m.

Films of this invention exhibit extremely good hot tack seal strength at temperatures in the range of from about 200° to 290° F. thereby rendering them extremely useful as packaging materials in high speed packaging operations.

15 Claims, No Drawings

SEALABLE POLYOLEFIN FILMS CONTAINING VERY LOW DENSITY ETHYLENE COPOLYMERS

FIELD OF THE INVENTION

This invention relates to laminar polyolefin film materials having a base layer comprising a blend of an olefin polymer and a very low density ethylene/alpha monoolefin copolymer and at least one heat sealable layer present on one or both surfaces of said base layer, said heat sealable layer comprising a very low density copolymer of ethylene and a different alpha monoolefin.

DESCRIPTION OF RELATED ART

Films based on polyolefin polymers and copolymers are widely used in packaging applications which require sealing of the film to itself as the package is formed and/or filled. This sealing may be accomplished using adhesives such as low density polyethylene, ethylene/vinyl acetate copolymers and the like. When heat sealing is used, it is important that the thermoplastic film be readily heat sealable while also maintaining other physical and mechanical properties such as resistance to tearing, tensile strength and processability in high speed packaging equipment.

In form/fill packaging operations, film is generally first processed into a bag, a bottom being formed by squeezing together two films, and subjecting the bottom to a temperature above the seal initiation temperature under pressure to seal the bottom of the bag. The bag is subsequently filled with the goods to be packaged, and the top is then sealed in a similar fashion.

Film heat sealing is generally affected by means of heated flat surfaces, between which film surfaces are forcefully pressed together at a temperature above the seal initiation temperature of the film. When use is made of equipment such as vertical form, fill and seal machines, the bag is filled with the contents to be packaged while the bottom seal is still hot. Cooling the seal would entail too long a waiting time, thus lengthening the cycle time and increasing operating costs. Consequently, the film must be one which enables the formation of a strong seal even as the seal formed is at or near the seal formation temperature, i.e., it must have good hot tack seal strength.

There are several other desirable characteristics of a heat sealable film which enable trouble free performance in form fill and seal applications. First the film should provide strong seals at a low temperature to minimize energy requirements. Additionally, the film should allow for strong seals over a broad temperature range so that the film is more forgiving of heat sealing equipment adjustments and inadequacies. And further, the film should enable the development of seal strength almost immediately (before cooling) so that the seal bears and secures the weight of the wrapped product.

Many commonly used plastic materials which are used in the formation of film products could benefit from an improvement of their heat sealing characteristics. For example, crystalline polyolefin films such as polypropylene films have found extensive use in the field of packaging. Polypropylene films, in both oriented or non-oriented form, are used widely in packaging applications because of their superiority in mechanical properties such as tensile strength, rigidity, surface hardness, and optical properties such as gloss and transparency, and in food hygiene properties such as freedom from toxicity and odor. However, polypropylene and other crystalline polyolefin films typically require heat sealing initiation temperatures upwards of about 120° C. before adequate film seal strengths (at least 200 g/inch, desirably 400 g/inch and higher per specified settings for pressure and dwell time) are obtained. Consequently, there has been considerable development work to find ways that would allow the heat sealing of polypropylene films at lower temperatures and provide good hot tack seal strength. Such approaches have included the use of coatings, blend components and multiple film layers.

For example, EPA 0221726 discloses a film laminate prepared by coextruding a base layer which may be a polyolefin, particularly polypropylene or mixtures of polyolefins, and a heat seal layer which may be a very low density polyethylene (VLDPE) or a blend thereof with another polyolefin. The reference also indicates that scrap film may be recycled which could lead to structures where the base layer would comprise a blend of polypropylene and VLDPE.

The VLDPE is described as having a density of 0.890 to 0.912 g/cc and a melt index of generally 0.8 g/10 minutes or less, and is said to be of low crystallinity and produced in a low pressure process.

EPA 0247897 discloses a film laminate comprising a base layer which may contain polypropylene and at least one heat-sealable film layer which may be based on a very low density copolymer of ethylene and an alpha-monoolefin such as octene-1.

U.S. Pat. No. 4,764,404 discloses a multi layer package film having adhered to one side of a base layer (aluminum, polyamide or vinylidene chloride sheet) a composition comprising a blend of polypropylene (40–70% by weight), a second component which may be a copolymer of ethylene and a different alpha olefin (5–35% by weight) and a third elastomeric olefin polymer or copolymer (10–40% by weight).

The second component may be ethylene-based copolymers available from Mitsui under the designations "TAFMER" A or P.

EPA 0341 091 discloses that certain linear low density ethylene copolymers made in accordance with U.S. Pat. No. 4,612,300 using a Ziegler-Natta magnesium halide supported catalyst have good heat seal properties for packaging applications. These copolymers may contain 7–40 wt % of a C_5 to C_{12} alpha olefin and exhibit a density of 0.87 to 0.915.

In addition, U.S. Pat. No. 4,291,092 and divisionals, U.S. Pat. Nos. 4,339,496, 4,340,640 and 4,340,641, all disclose a heat sealable packaging film layer for a polypropylene substrate wherein the film layer comprises a blend of a copolymer of ethylene and a higher olefin and a copolymer of propylene and a higher olefin. U.S. Pat. No. 4,643,945 discloses the use of a linear low density polyethylene in a heat sealable film composition.

The prior art heat sealable films are not without certain deficiencies. A need still exists in the industry for a heat sealable layer having a seal initiation temperature of about 110° C. (225° F.) or lower while the film maintains good elevated temperature hot tack properties, abrasion resistance, blocking resistance, good strength and rigidity, and good film optical properties.

A class of highly active olefin catalysts known as metallocenes is well known especially in the preparation of polyethylene and ethylene copolymers. These catalysts, particularly those based on group IV B transi-

tion metals such as zirconium, titanium and hafnium, show extremely high activity in ethylene polymerization. The metallocene catalysts are also highly flexible in that, by manipulation of catalyst composition and reaction conditions, they can be made to provide polyolefins with controllable molecular weights from as low as about 200 (useful in applications such as lube oil additives) to about 1 million or higher as, for example, ultra high molecular weight linear polyethylene. At the same time, the molecular weight distribution of the polymers can be controlled from extremely narrow (as in a polydispersity, M_w/M_n of about 2), to broad (a polydispersity of about 8).

Exemplary of the development of these metallocene catalysts for the polymerization of ethylene is found in U.S. Pat. No. 4,937,299 to Ewen et al., hereby incorporated herein by reference. Among other things, this patent teaches that the structure of the metallocene catalyst includes an alumoxane which is formed when water reacts with trialkyl aluminum with the release of methane, which alumoxane complexes with the metallocene compound to form the catalyst.

There are a number of structural variables in polyolefins which affect the ultimate properties of the polymer. Two of the most important are composition distribution (CD) and molecular weight distribution (MWD). Composition distribution (CD) refers to the distribution of comonomer between copolymer molecules. This feature relates directly to polymer crystallizability, optical properties, toughness and many other important use characteristics. Molecular weight distribution (MWD) plays a significant role in melt processability as well as the level and balance of physical properties achievable. Molecular weight (MW) determines the level of melt viscosity and the ultimately desired physical properties of the polymer. The type and amount of comonomer effects the physical properties and crystallizability of the copolymer. All of these structural features (MW, MWD, CD, comonomer type and amount) are readily controllable through he use of metallocene catalysts as exemplified in U.S. Pat. No. 4,937,299, cited above.

Metallocene catalyst are particularly attractive in making tailored ultrauniform and super random specialty copolymers. For example, if a lower density ethylene copolymer is made with a metallocene catalyst, such as very low density polyethylene (VLDPE), an ultrauniform and super random copolymerization will occur, as contrasted with the polymer produced by copolymerization using a conventional Ziegler catalyst.

SUMMARY OF THE INVENTION

The invention provides laminar polyolefin film materials having a base film layer comprising a blend of an olefin polymer and up to about 30% by weight of at least one very low density copolymer of ethylene and a C_3 to C_{20} alpha monoolefin comonomer copolymerizable with ethylene, said base layer having a heat sealable film layer present on one or both surfaces thereof comprising a very low density copolymer of ethylene and a copolymerizable C_3 to C_{20} alpha olefin comonomer, said film further characterized in that the ethylene/alpha monoolefin copolymer present in one of said layers is a copolymer of ethylene and a C_6 C_{10} alpha monoolefin which alpha monoolefin differs from the alpha monoolefin present in the ethylene copolymer of the other said layers. The ethylene copolymer constituents of the film are characterized as having a density in the range of about 0.88 g/cm^3 to abut 0.915 g/cm^3, a melt index in the range of about 0.5 dg/min to about 7.5 dg/min, a molecular weight distribution (M_w/M_n) of about 1.5 to about 3.5 and an essentially single melting point in the range of about 60° C. to about 115° C., measured as a DSC peak T_m.

Films of this invention exhibit extremely good hot tack seal strength at temperatures in the range of from about 200° to 290° F. thereby rendering them extremely useful as packaging materials in high speed packaging operations.

DETAILED DESCRIPTION OF THE INVENTION

The polyolefin component of the base (or core) material of the film of this invention is preferably selected from the group consisting of polypropylene, low density polyethylene, linear low density polyethylene, polybutene, random copolymers of propylene with up to about 15 mole % of a C_2 or C_4 to C_{12} alpha olefin as well as blends of two or more of these materials. The polyolefins which may be used as the major component in the base layer are distinguished from the VLDPE copolymers also contained in the film in that the former generally exhibit a density in excess of about 0.915 g/cm^3.

The preferred polyolefin component of the base layer is crystalline polypropylene or random copolymers of propylene and another alpha olefin. Where random propylene copolymers are used as the base layer, the content of propylene is preferably in the range of from about 88 to 99 mole percent, based on total moles, more preferably in the range of about 90 mole percent to about 94 mole percent. The preferred random copolymers consist of propylene copolymerized with about 1 to 10 mole percent of ethylene.

The VLDPEs which may be used as the copolymer component of the base or sealing layers of the film of this invention are ethylene/alpha-monoolefin copolymers wherein the monoolefin can have from 3–20 carbon atoms such as ethylene/butene-1, ethylene/hexene-1, ethylene/octene-1, ethylene/propylene copolymers. These ethylene copolymers with prescribed range of comonomer levels can be prepared by polymerization of the suitable olefins in the presence of supported or unsupported metallocene catalysts systems. The preferred range of comonomer level generally ranges from about 4 to about 15 mole percent.

The low melting polymer ingredient utilized in the base layer and heat seal layer of the film of the present invention has a density in the range of about 0.88 g/cm^3 to about 0.915 g/cm^3. Preferably the density is in the range of about 0.89 g/cm^3 to about 0.91 g/cm^3. Densities above about 0.90 g/cm^3 are measured using standard accepted procedures. At densities below about 0.90 g/cm^3, the samples are additionally conditioned by holding them for 48 hours at ambient temperature (23° C.), prior to density measurement.

The melt index (MI) of the ethylene/alpha-monoolefin copolymers of the present invention is in the range of about 0.5 dg/min to about 7.5 dg/min. Preferably the MI is in the range of about 0.5 dg/min to about 5.0 dg/min, and the most preferred MI is in the range of 1.0 to 2.5 dg/min. MI as measured herein is determined according to ASTM D-1238 (190/2.16). High load MI is determined according to ASTM D-1238 190/21.6). These copolymers also have a narrow molecular weight distribution. The ratio of M_w/M_n is generally in the

range of about 1.5 to about 3.5, preferably in the range of about 2.0 to about 3.0.

The ethylene/alpha-monoolefin copolymers should also have an essentially single melting point characteristic with a peak melting point (T_m) as determined by Differential Scanning Colorimetry (DSC) in the range of about 60° C. to about 115° C. Preferably the DSC peak T_m is in the range of about 80° C. to about 100° C. "Essentially single melting point" as used herein means that at least about 80% by weight of the material corresponds to a single T_m peak existing in the range of about 60°–115° C., and there is essentially absent from the polymer any substantial fraction of material which corresponds to a T_m peak found at a temperature higher than about 115° C. i.e., "essentially" the bulk material content of the polymer corresponds to a "single" melting point peak in the 60°–115° C. range, and "essentially" no substantial fraction of the material has a peak melting point in excess of about 115° C., as determine by DSC analysis.

DSC measurements are made on a perkin Elmer System 7 Thermal Analysis System. Melting information reported are second melting data i.e. the sample in heated at a programmed rate of 10° C./min to a temperature above its melting range. The sample is then cooled at a programmed rate of 10° C./min to a temperature below its crystallization range. The sample is then reheated (2nd melting) at a programmed rate of 10° C./min.

The presence of higher melting peaks is detrimental to film properties such as haze, and compromises the chances for meaningful reduction in the seal initiation temperature of the final film.

The composition distribution breadth index (CDBI) of such VLDPE copolymers will generally be in the range of about 70 percent or higher. The CDBI is defined as the weight percent of the copolymer molecules having a comonomer content within 50 percent (i.e. ±50%) of the median total molar comonomer content. The CDBI of linear polyethylene, which does not contain a comonomer, is defined to be 100%.

The Composition Distribution Breadth Index (CDBI) is determined via the technique of Temperature Rising Elution Fractionation (TREF). CDBI determination clearly distinguishes the VLDPE copolymers of this invention (narrow composition distribution as assessed by CDBI values generally above 70%) from VLDPEs available commercially today which generally have a broad composition distribution as assessed by CDBI values generally less than 55%. The benefits to the subject invention accrue through the specific use of VLDPEs of narrow composition distribution. The CDBI of a copolymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation as described, for example, Wild et al., *J. Poly. Sci, Poly, Phys. Ed., Vol.*, 20, p. 441 (1982). Unless otherwise indicated, terms such as "comonomer content", "average comonomer content" and the like refer to the bulk comonomer content of the indicated copolymer.

Utilizing a metallocene catalyst, the VLDPE copolymers useful as the low melting polymers of the present invention can be produced in accordance with any suitable polymerization process, including a slurry polymerization, gas phase polymerization, and high pressure polymerization process.

A slurry polymerization process generally uses superatomospehric pressures and temperatures in the range of 40°–100° C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The liquid employed in the polymerization medium can be an alkane, cycloalkane, or an aromatic hydrocarbon such as toluene, ethylbenzene or xylene. The medium employed should be liquid under the conditions of polymerization and relatively inert. Preferably, hexane or toluene is employed.

Alternatively, the VLDPE copolymer components of the present invention may be formed by gas-phase polymerization. A gas-phase process utilizes superatmospheric pressure and temperatures in the range of about 50°–120° C. Gas phase polymerization can be performed in a stirred or fluidized bed of catalyst and product particles in a pressure vessel adapted to permit the separation of product particles from unreacted gases. Ethylene, comonomer, hydrogen and an inert diluent gas such as nitrogen can be introduced or recirculated so as to maintain the particles at a temperatures of 50° C.–120° C. Triethylaluminum may be added as needed as a scavenger of water, oxygen, and other impurities. Polymer product can be withdrawn continuously or semicontinuously at a rate such as to maintain a constant product inventory in the reactor. After polymerization and deactivation of the catalyst, the product polymer can be recovered by any suitable means. In commercial practice, the polymer product can be recovered directly from the gas phase reactor, freed of residual monomer with a nitrogen purge, and used without further deactivation or catalyst removal.

The VLDPE copolymers of the present invention can also be produced in accordance with a high pressure process by polymerization ethylene in combination with other monomers such as butene-1, hexene-1, octene-1, or 4-methylpentene-1 in the presence of the catalyst system comprising a cyclopentadienyl-transistion metal compound and an alumoxane compound. It is important, in the high-pressure process, that the polymerization temperature be above about 120° C. but below the decomposition temperature of the polymer product and that the polymerization pressure be above about 500 bar (kg/cm^2). In those situations wherein the molecular weight of the polymer product that would be produced at a given set of operating conditions is higher than desired, any of the techniques known in the art for control of molecular weight, such as the use of hydrogen or reactor temperature, may be used in the process of this invention.

The blend composition of the film base layer contains from about 1 to about 30 percent by weight of the VLDPE copolymer component, more preferably from about 5 to abut 25 percent by weight of VLDPE, each based on the total weight of olefin polymer forming the base film layer.

The VLDPE copolymer which is applied to one or both surfaces of the base film layer to form a heat sealable layer possesses the same physical and chemical characteristics and may be made by the same processes as described above with respect to the VLDPE component of the base layer, except that it differs compositionally from the copolymers contained in the base layer.

It has been found that the excellent results in terms of hot tack seal strength are achieved where the VLDPE component of a first layer which may be the base layer or heat sealable layer is a copolymer of ethylene and a C_3 to C_{20} alpha-monoolefin and the VLDPE compo-

nent of the other layer is a copolymer of ethylene and a C_6 to C_{10} alpha-monoolefin which differs from the alpha-monoolefin comonomer present in the VLDPE of the first layer. In the more preferred embodiments of the invention, the C_6 to C_{10} alpha-monoolefin-containing copolymer is used as the heat seal layer and the different C_3 to C_{20} alpha-monoolefin-containing copolymer is used as a component in the base layer.

These materials provide an excellent balance of adhesion to the substrate base film without the need to employ an interdisposed anchor or tie layer such as polyvinylidene chloride or ethylene/vinyl acetate copolymers, and also possess the requisite high hot tack seal strength required for modern high speed packaging applications. Best results in terms of adhesion and hot tack seal strength are achieved with laminar structures wherein the VLDPE copolymer component of the base layer is an ethylene/butene-1 copolymer and the heat seal coating layer comprises a copolymer of ethylene with either hexene-1 or octene-1.

The percent hexane extractables for the low melting polymer VLDPE ingredients of the present invention are low enough to allow for applications in the food industry. Preferably, for food packaging applications, products having extractables 5 percent and under would be utilized.

The heat sealable films of the present invention may be manufactured using film fabrication technologies well known in the art. For example, the base film may be extruded into film using a flat die or blown extruded into film using a tubular die, and the heat seal layer formed thereon by solvent deposition, lamination or coextrusion techniques. A preferred method of manufacture is via coextrusion wherein a molten layer of the heat seal material is applied to the surface of an extruded cast film of the base layer. These laminar films may optionally be further oriented (either uniaxially or biaxially) using technologies well known to those skilled in the art.

The laminar film structure of the present invention may have an overall thickness in the range of from about 0.5 mil to about 5 mil, with a preferred thickness of about 0.75 mil to about 2.5 mil. The heat seal coating layer may constitute from about 3 to about 50% of this overall thickness, more preferably from about 10 to 25% of the overall thickness, present on one or both sides of the base layer.

The VLDPE copolymer component of the base layer may also comprise a mixture of compositionally different VLDPE components within the scope of this invention. This is particularly the case because the VLDPE component of the base layer differs compositionally from the VLDPE component of the heat seal layer. Scrap trim recycled to the extruder and mixed with virgin polymer used to make the base layer will result in a base layer which contains a mixture of these VLDPE copolymers. Thus, in a preferred embodiment wherein the heat sealable layer comprises a VLDPE copolymer of ethylene and hexene-1 and the base layer contains a VLDPE copolymer of ethylene and butene-1, recycle of scrap trim back to the extruder would result in a base layer containing a mixture of the ethylene/butene-1 and ethylene/hexene-1 copolymers, along with the major polyolefin component of the base layer.

The polymer components used to fabricate the films of the present invention may also contain appropriate amounts of other additives normally included in such compositions. These include slip agents such as talc, antioxidants, fillers, dyes, pigments, radiation stabilizers and like additives.

The film products made in accordance with the present invention are useful in a wide variety of bag and pouch applications in which heat sealability is important. Bag and pouch forming include, but are not limited to horizontal form-fill-and-seal, and vertical form-fill-and-seal.

Some key properties of the final film are heat sealability and seal strength, hot tack strength, tensile strength, film rigidity, haze and gloss, low extractables, and abrasion resistance.

EXAMPLES

Example I

Preparation of VLDPE-EB-1 (1.6 MI, Density of 0.8895, butene-1 Comonomer)

A catalyst is prepared by adding 5.1 liters of a 10% solution of trimethylaluminum in heptane into a dry and oxygen-free two-gallon reactor equipped with a mechanical stirrer. 800 g of undehydrated silica gel, containing 12.3% water, is slowly added into the reactor. After the addition is complete, the mixture is stirred at ambient temperature for one hour. 20 g of di-(n-butylcyclopentadienyl) zirconium dichloride slurried in 30 liters of heptane is then added into the reactor and the mixture is allowed to react at ambient temperature for 30 minutes. The reactor is then heated to 65° C., while a nitrogen gas is purged through the reactor to remove the solvent. The nitrogen purging is stopped when the mixture in the reactor turns into a free-flowing powder.

The polymerization was conducted in a 16-inch diameter fluidized gas phase reactor. Ethylene, butene-1 and nitrogen were fed continuously into the reactor to maintain a constant production rate. Product was periodically removed from the reactor to maintain the desired bed weight. The polymerization conditions are shown below.

Gas Phase Polymerization	
Temperature (°F.)	137
Total Pressure (psia)	300
Gas Velocity (ft/sec)	1.58
Catalyst Feed Rate (g/hr)	7.0
Butene-1 Feed Rate (lb./hr)	5.3
Production Rate (lb/hr)	26

The polymerized product had a Melt Index (dg/min.) of 1.60 and a Density (g/cm^3) of 0.8895.

Example 2

Preparation of VLDPE-EB-2 (2.3 MI, Density of 0.8970, butene-1 comonomer)

The process of Example 1 was repeated as set forth therein except that the polymerization conditions were as shown below:

Gase Phase Polymerization	
Temperature (°F.)	129
Total Pressure (psia)	300
Gas Velocity (ft/sec)	1.59
Catalyst Fed Rate (g/hr)	7.0
Butene-1 Feed Rate (lb./hr)	2.9
Production Rate (lb./hr)	19

The polymerized product had a Melt Index (dg/min.) of 2.30 and a Density (g/cm^3) of 0.8970.

Example 3

Preparation of VLDPE-EH (15 MI, Density of 0.905, hexene-1 comonomer)

The catalyst for polymerizing this ethylene copolymer was prepared as follows: An 800 gram quantity of silica gel and a 2700 ml. aliquot of methylalumoxane/-toluene solution (10%) were placed in a two-gallon reactor and allowed to react at ambient temperature for one hour. A 21.6 gram quantity of di-(n-butylcyclopentadienyl) zirconium dichloride slurried in 300 ml of toluene was added into the reactor and the mixture was allowed to react at 65° C. for 30 minutes. The reactor was then heated at 75° C. while nitrogen gas was purged through the reactor to remove the solvent. The heating and nitrogen purging were stopped when the mixture in the reactor turned into a free-flowing powder.

The polymerization was conducted in a 16-inch diameter fluidized bed gas-phase reactor. ethylene, hexene-1 and nitrogen were fed continuously into the reactor to maintain a constant production rate. Product was periodically removed from the reactor to maintain the desired bed weight. The polymerization conditions are shown below:

Gas Phase Polymerization	
Temperature (°F.)	158
Total Pressure (psia)	300
Gas Velocity (ft/sec)	1.22
Catalyst Feed Rate (g/hr)	3.0
Hexene-1 Feed Rate (lb./hr)	3.1
Production Rate (lb./hr)	20

The polymerized product had a measured Melt Index (dg/min) of 1.5 and a density of 0.905 g/cm^3.

Examples 4–12

A series of coextruded unoriented films were produced on a compounding extruder to produce AB type laminar films comprising a base film layer having an average thickness of 1.6 mil and a single heat sealable coating layer having an average thickness of 0.4 mils, i.e., the coating layer constituted about 20% of the thickness of the composite film. The composition of the base films was either polypropylene, a propylene/ethylene random copolymer or a mixture of one of the above with a VLPDE copolymer of ethylene and butene-1 as prepared in Examples 1 and 2. The composition of the coating layer was either a VLDPE copolymer of ethylene and butene-1 or a VLDPE copolymer of ethylene and hexene-1 as prepared in accordance with Example 3. The composition of these various layers is identified in Table 1.

As used in Table "PEC" is a crystallizable random copolymer of propylene having a MFI of 5.0 dg/min and containing abut 5 wt % ethylene. It has a DSC peak melting temperature of about 132° C. and is available commercially from Exxon Chemical Company as Exxcorene TM PD-9282. PP is a crystallizable polypropylene homopolymer having an MFI of about 2.3 dg/min and is available from Exxon Chemical Company under the designation Exorcene TM PP4092. The material identified as EB-1 is a VLDPE copolymer of ethylene and butene-1 as prepared in Example 1 having a MFI of 1.60 dg/min and a density of 0.8895 g/cm^3. The material designated as EB-2 is a VLDPE prepared in Example 2 with a MFI of 2.30 dg/min and a density of 0.8970 g/cm^3. The material designated EH is a VLDPE copolymer of ethylene and hexene-1 as prepared in Example 3 having an MFI of 1.5 dg/min and a density of 0.905 g/cm^3.

The material designated EVA is a copolymer of ethylene and vinyl acetate (28% by weight vinyl acetate content) having an MFI of 3.1 dg/min.

Heat seal data and hot tack seal strengths of the various film formulations and configurations were evaluated using a Thellar Model EB Heat Sealer. Under this test, the heat seal sides of the coated films are brought into contact and seals are attempted to be formed at various temperatures from 140° F. to 300° F. in 10°F. increments. The dwell time and pressures applied during sealing generally ranges from about 0.25 to 0.5 seconds and 65–80 psi respectively. The times and pressures employed are indicated in Table 1.

Test results are shown in Table 1. As is evident from the data in Table 1, film compositions within the scope of this invention (Examples 8 and 9) exhibited hot tack strengths in excess of 625 g/in over a sealing temperature of 240° to 270° F. and over 700 g/in at sealing temperatures of 240° F. This is in marked contrast to other formulations outside the scope of the present invention wherein the sealing layer and base layer each contain a VLDPE copolymer of ethylene and butene-1 or a copolymer of ethylene and vinyl acetate.

TABLE 1

EXAMPLE	BASE FILM COMPOSITION		VLDPE COATING COMPOSITION	DWELL TIME (SEC)	SEAL PRESSURE (PSI)	SEAL STRENGTH (g/IN) AT °F. 200°	210°	220°	230°	240°	250°	260°	270°
4	100% PEC	—	EB-1	0.5	67	<25	<25	25	<25	<25	<25	<25	<25
5	80% PEC	20% EB-1	EB-1	0.5	70	25	25	<25	<25	<25	<25	<25	<25
6	80% PP	20% EB-1	EB-1	0.5	70	NS*	NS	<25	25	<25	<25	<25	<25
7	100% PEC	—	EB-2	0.5	70	NS	<25	<25	<25	<25	<25	<25	<25
8	100% PP	—	EB-2	0.5	67	NS	<25	25	25	75	25	25	25
9	80% PP	20% EB-1	EH	0.25	70	NS	100	425	>700	>700	>700	>700	>700
10	80% PP	20% EB-1	EH	0.5	76	25	225	375	550	>700	625	675	675
11	100% PEC	—	EVA	0.5	70	(MAX SEAL STRENGTH AT 160° F.; <25 ABOVE 200° F.)							
12	100% PEC	—	EVA	0.25	70	(MAX SEAL STRENGTH AT 170° F.; <75 ABOVE 200° F.)							

*NS MEANS NO SEAL

I claim:

1. A multiple layer heat sealable film comprising a base layer and a heat sealable layer superimposed on one or both sides of said base layer;

said base layer comprising a blend of (a) an olefin polymer having a density in excess of 0.915 g/cm^3 and (b) from about 1 to about 30 weight percent based on base layer polymer content of a copolymer of ethylene and a C_3 to C_{20} alpha monoolefin comonomer, said copolymer having a density of from about 0.88 to about 0.915 g/cm^3, a melt index of from about 0.5 to about 7.5 dg/min, a molecular weight distribution of no greater than about 3.5 and a composition distribution breadth index greater than about 70 percent;

said heat sealable layer comprising a copolymer of ethylene and a C_3 to C_{20} alpha-monoolefin comonomer, said copolymer having a density of from about 0.88 to about 0.915 g/cm^3, a melt index of from about 0.5 to about 7.5 dg/min, a molecular weight distribution of no greater than about 3.5 and a compositional breath index greater than about 70 percent, said film further characterized in that the ethylene/alpha-monoolefin copolymer present in one of said layers is a copolymer of ethylene and a C_6 to C_{10} alpha-monoolefin which alpha-monoolefin differs from the alpha-monoolefin comonomer present in the copolymer of the other said layers.

2. The film of claim wherein said copolymer of ethylene and C_6 to C_{10} alpha-monoolefin is present in said heat sealable layer.

3. The film of claim 2 wherein said film has a thickness in the range of from about 0.5 to about 5.0 mils.

4. The film of claim 2 wherein said heat sealable layer constitutes about 3 to about 50% of the thickness of said film.

5. The film of claim 2 wherein said ethylene copolymer present in each layer contains from about 4 to about 15 mole percent of said comonomer.

6. The film of claim 2 wherein said heat sealable layer comprises a copolymer of ethylene and hexene-1.

7. The film of claim 6 wherein said base layer comprises a copolymer of ethylene and butene-1.

8. The film of claim 2 wherein the olefin polymer component of said base layer is selected from the group consisting of polypropylene, random copolymers of propylene with up to about 15 mole % of a C_2 or C_4–C_{12} alpha olefin, low density polyethylene, linear low density polyethylene, high density polyethylene, polybutene and mixtures thereof.

9. The film of claim 8 wherein the olefin polymer component of said base layer is polypropylene.

10. The film of claim 8 wherein the olefin polymer component of said base layer is a crystallizable random copolymer of propylene and ethylene.

11. The film of claim 2 wherein each of said ethylene copolymers present in said base layer and said heat sealable layer are prepared using a metallocene catalyst system.

12. The film of claim 2 wherein said heat sealable layer is superimposed on only one side of said base layer.

13. The film of claim 12 wherein said heat sealable layer comprises about 20% of the thickness of the composite film.

14. A process for fabricating a heat sealed package comprising contacting the surfaces of the heat sealable layers of a film in accordance with claim 1 with one another and under conditions of temperature and pressure sufficient to bond said heat sealable layers together.

15. The process of claim 14 wherein said temperature ranges from about 210° to about 270° F.

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(54) Title: LINEAR ETHYLENE INTERPOLYMER BLENDS OF INTERPOLYMERS HAVING NARROW MOLECULAR WEIGHT AND COMPOSITION DISTRIBUTIONS

(57) Abstract

Linear ethylene interpolymer blends are disclosed. The blends are made from components having a narrow molecular weight distribution (e.g. $M_w/M_n \leq 3$) and a narrow composition distribution (e.g. CDBI > 50 %). The blend components in a blend can all have the same molecular weight but different comonomer contents, the same comonomer content but different molecular weights, or comonomer contents which increase with molecular weight. The blends have either $M_w/M_n > 3$ or CDBI < 50 %, or both, and can be multimodal with respect to either or both molecular weight and/or comonomer content. The blends are generally free of blend components having both a higher average molecular weight and a lower average comonomer content than another blend component. The blends can have improved mechanical, physical and/or chemical properties.

